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XC. *On some Radio-Frequency Properties of Ionized Air.*

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1. *Introduction.*

THE experimental investigations described in the present paper were carried out with the aim of elucidating by laboratory experiments the rôle played by ionized air in wireless-wave propagation. Interest in such experiments dates back to the British Association discussion of 1912, in which Dr. Eccles gave an account of his ionic refraction theory †, according to which the bending of wireless waves round the earth is attributed to an increased phase velocity brought about in the upper atmosphere by the presence of ions. As a result of the discussion the late Professor E. H. Barton, at the suggestion of Professor J. A. Fleming, began an experimental investigation of the effect of ionization on the conductivity and dielectric constant of ionized gas for high frequency electromotive forces. Theory indicates that, for conditions under which the phase velocity of electric waves of a particular frequency is increased by the presence of ions, the dielectric constant of the medium should be less than unity for alternating electromotive forces of the same frequency.

* Communicated by the Authors.

† *Vide* Proc. Roy. Soc. A, lxxxvii. pp. 79–99 (1912).

Barton and Kilby *, using gaseous ionization produced at atmospheric pressure by X-rays or radium bromide, were able to detect, by high frequency methods, the effect of the conductivity of the gas ; but they did not consider that their results indicated a diminution of the dielectric constant of the gas. Their experimental apparatus included an oscillatory circuit in which the condenser consisted of two plates between which the ionization was produced. Variations of apparent capacity were found, which were attributed to the effects of the conductance of the gas acting as a leak in parallel with the condenser. It was shown that the effect of such a leak would be to alter the natural frequency of an oscillatory circuit, and the variations of apparent capacity were attributed to this effect. But the experimental arrangement used by Barton and Kilby was such that *forced* and not *free* vibrations were produced in the oscillatory circuit, and we think their work requires another interpretation. When this is done it will be seen that these authors probably did detect experimentally the reduction of the dielectric constant below unity—in other words, it is possible that their experiment was more successful than they thought.

The same problem of the dielectric constant of ionized gas was later attacked by van der Pol †, who used very short damped waves to energize a Lecher wire system. The effect of introducing the ionized gas of a glow discharge between two small electrodes at the end of the Lecher wire system was compared with the effect of introducing common salt solution of the same conductivity. The apparent dielectric constant of the ionized gas was examined at different pressures, and found to be sometimes greater than unity, sometimes indistinguishable from unity, and at very low pressures definite evidence of a dielectric constant less than unity was found. Van der Pol attributed the increase of the dielectric constant beyond unity to inhomogeneity in the gas between the condenser plates. In this connexion it may be mentioned that Barton and Kilby had previously found an apparent increase of the dielectric constant but they had regarded the effect as spurious and due to the effect of the conductance of the gas on the circuit tuning.

The present series of investigations was begun in 1922 at Cambridge by Captain A. G. D. West and one of the authors. It had been found theoretically that by tuning an oscillatory circuit to *potential* resonance and not to *current* resonance the difficulties usually introduced by shunting the oscillatory

* Phil. Mag. [6] xxvi. p. 567 (1913).

† Thesis, University of Utrecht (1920).

circuit condenser by a resistance could be entirely avoided, so that the problem of measuring the dielectric constant could be attacked in a new way.

In the experiments carried out at Cambridge in 1922, which are described briefly below, a definite diminution of the dielectric constant was found, confirming van der Pol's result, although the wave-lengths used were of quite a different order of magnitude. This effect was found chiefly at low pressures and very low ionic concentrations. With higher concentrations the dielectric constant assumed values greater than unity, so that the discrepancy of theory and experiment still remained although the experimental conditions were widely different from those of Barton and Kilby, on the one hand, and from those of van der Pol on the other. In this connexion it should be mentioned that the theoretical expression for the dielectric constant of ionized gas does not permit values greater than unity whatever the ionic concentration may be.

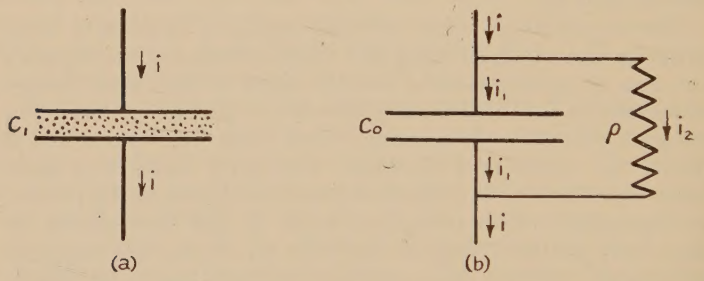
The experiments were resumed again in London in 1925 with the aim of elucidating the above-mentioned discrepancy and also of testing various modifications of the ionic theory of refraction that had been proposed in the meantime. For example, Sir Joseph Larmor * had then just published a theory in which free electrons with long mean free paths were considered as the effective electrical agents in the process of atmospheric wave deviation, while it had been shown by one of the writers † that, if this were so, the earth's magnetic field would produce the magneto-optic phenomena of double refraction and rotary polarization. If the effective carriers are ions of molecular mass no such magnetic effects are to be expected for wave-lengths within the wireless spectrum. In the experiments carried out to test this point, which are described below, magneto-optic resonance corresponding to the Inverse Zeeman effect has been found, thus demonstrating that we must regard free electrons as producing the reduction of dielectric constant. An account is also given of experiments which explain the increase of apparent dielectric constant quantitatively as well as qualitatively.

Within the last few years papers on the subject of the dielectric constant of ionized gas have been published by Gutton ‡, Bergmann and Düring §, Szekely ‖, and Benner ¶.

* Larmor, Phil. Mag. [6] xlviii. no. 228, p. 1025 (1924).
† Appleton, Proc. Phys. Soc. xxxvii. part 2 (Feb. 15th, 1925).
‡ *Annales da Physique*, xiii. p. 62 (1930).
§ *Annalen der Physik*, v. Bd. i. no. 8, p. 1041 (1929).
‖ *Annalen der Physik*, v. Bd. iii. no. 1, p. 112 (1929).
¶ *Die Naturwissenschaften*, xvii. p. 120 (1929).

Gutton found a diminution of the dielectric constant for low ionic concentrations, but at higher concentrations he found an apparent increase of dielectric constant. From his results Gutton has concluded that the electrical carriers in ionized gas cannot be regarded as free, and that they possess a natural frequency, due to the existence of quasi-electric forces, which is proportional to $N^{3/8}$, where N is the number of electric charges per c.c. This result, if true, would completely revolutionize our ideas as to the mechanism of the atmospheric deviation of wireless waves, and therefore demands a careful examination. Bergmann and Düring have demonstrated the important and significant result that when there are only electrons between the condenser plates an increase in the dielectric constant is not observed, complete agreement with the simple theory (which predicts a

Fig. 1.



dielectric constant decreasing steadily with increase of N) being found. Szekely, in an experiment mainly devoted to the measurements of absorptive effects, found evidence of an increase of apparent dielectric constant.

2. *The Measurement of the Dielectric Constant of a Conducting Ionized Medium.*

The effect of ionizing the air between the plates of a condenser is equivalent to altering the values of the capacity of the condenser and at the same time inserting a high resistance leak in parallel. In order to obtain the relationship between the dielectric constant and the degree of ionization of the medium (air) let us consider the equivalent circuits (figs. 1 *a* and 1 *b*). C_1 is the capacitance of the leaky condenser, whose dielectric is ionized air, which may be considered as being electrically equivalent to a perfect condenser of capacitance C_0 in parallel with a resistance ρ.

Let A be the area of the condenser plates in both cases and d the distance between them. Let V be the instantaneous value of the alternating potential difference across the plates. The electric field in both cases is given by V/d. We now consider each case separately.

Circuit 1 *a*.

Let us assume that the ionized medium contains N electrons per c.c. each of charge e and mass m. If x is the displacement of the electrons under the influence of the alternating electric field E, we have

$$m\frac{d^2x}{dt^2}+g\frac{dx}{dt}=\mathrm{E}e, \quad . \quad . \quad . \quad . \quad (1)$$

where g is a frictional constant. If E is sinusoidal in form (*e.g.*, $\mathrm{E}_0 \sin pt$) we find that

$$\frac{dx}{dt}=v=\left(\frac{eg}{m^2p^2+g^2}\right)\mathrm{E}-\left(\frac{me}{m^2p^2+g^2}\right)\frac{d\mathrm{E}}{dt}. \quad . \quad . \quad (2)$$

Now for the current through A units of area of cross-section we have, generally,

$$i=\mathrm{A}\left(\mathrm{N}ev+\frac{1}{4\pi}\frac{d\mathrm{E}}{dt}\right), \quad . \quad . \quad . \quad . \quad . \quad (3)$$

so that, on substituting for v from (2), we have

$$i=\left(\frac{\mathrm{AN}e^2g}{m^2p^2+g^2}\right)\mathrm{E}+\frac{\mathrm{A}}{4\pi}\left(1-\frac{4\pi\mathrm{N}e^2m}{m^2p^2+g^2}\right)\frac{d\mathrm{E}}{dt}. \quad . \quad (4)$$

Circuit 1 *b*.

Here we have (see figure)

$$i=i_1+i_2=\frac{\mathrm{V}}{\rho}+\mathrm{C}_1\frac{d\mathrm{V}}{dt},$$

or

$$i=\frac{d}{\rho}\mathrm{E}+\mathrm{C}_1d\frac{d\mathrm{E}}{dt}. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Now, since the two systems are to be considered as electrically equivalent, we may equate the coefficients of E and $\frac{d\mathrm{E}}{dt}$ in (4) and (5). We then get

$$\frac{d}{\rho}=\frac{\mathrm{AN}e^2g}{m^2p^2+g^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and

$$\mathrm{C}_1d=\frac{\mathrm{A}}{4\pi}\left(1-\frac{4\pi\mathrm{N}e^2m}{m^2p^2+g^2}\right). \quad . \quad . \quad . \quad . \quad (7)$$

But $\frac{A}{4\pi d} = C_0$, and $\rho = \frac{d}{A\sigma}$, where σ is the conductivity of the medium, so that we have from (6) and (7)

$$C_1 = C_0\left(1 - \frac{4\pi N e^2 m}{m^2p^2 + g^2}\right), \quad . \quad . \quad . \quad . \quad (8)$$

$$\sigma = \frac{d}{\rho A} = \frac{N e^2 g}{m^2p^2 + g^2}. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

We thus see that the introduction of the ionized gas between the plates of a given condenser is equivalent to diminishing the dielectric constant by $\frac{4\pi N e^2 m}{m^2p^2 + g^2}$, at the same time adding a leak in parallel of magnitude given by ρ in (9) *. The problem of investigating the high-frequency behaviour of ionized gas, then, resolves itself into the measurement of the dielectric constant of a conducting medium obeying Ohm's law.

3. *The Elimination of the Conductance Effect.*

In his experiments on the dielectric constant of a glow discharge van der Pol allowed for the effect of leakage on the conditions of resonance by a series of check experiments, using salt solution in place of ionized gas. In this case it had to be assumed that the dielectric constant of the salt solution was constant when the concentration and therefore the conductivity was varied. In the experiments described here the effect of the conductance of the gas on the "tuning" of the oscillatory circuit, of which the experimental condenser formed a part, has been eliminated. This was found to be possible by using an electrostatic voltmeter to determine the value of capacity for which the resonance voltage is obtained. The theory of this method is outlined very briefly below.

Let us consider the effect of the impression of an electromotive force $E_0 \sin pt$ on the oscillatory circuit represented diagrammatically in fig. 2. We assume that reaction from the oscillatory circuit on the generator is negligible.

* In the above calculation the ionization has been assumed small and the usual Lorentz local polarization term has not been introduced.

To introduce this term, however, it is only necessary to replace m in (8) and (9) by $\left(m + \frac{4\pi}{3}\frac{Ne^2}{p^2}\right)$.

As the expression for Kirchhoff's laws for the oscillatory circuit we have

$$L\frac{di_1}{dt}+Ri_1-E_0\sin pt=\int\frac{i_2dt}{C}=-v,$$

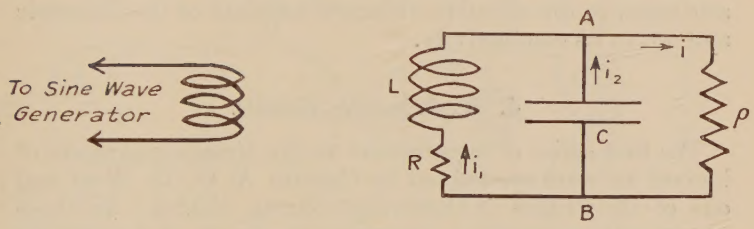
and

$$i=i_1+i_2=\frac{v}{\rho},$$

where R is the ohmic resistance of the coil L, ρ the non-inductive resistance (*e.g.*, of ionized gas) in parallel with the condenser C, and v the instantaneous voltage between the points A and B. These equations may be combined in the representative differential equation

$$\frac{d^2v}{dt}+\left(\frac{R}{L}+\frac{1}{\rho C}\right)\frac{dv}{dt}+\frac{1}{LC}\left(1+\frac{R}{\rho}\right)v=\frac{E_0}{LC}\sin pt, \quad . \quad (10)$$

Fig. 2.



the particular integral of which is given by

$$v=A\sin(pt-\theta),$$

where

$$A=\frac{E_0}{LC\sqrt{\left(\frac{R}{L}+\frac{1}{C}\right)^2p^2+\left(\frac{1}{LC}\left(1+\frac{R}{\rho}\right)-p^2\right)^2}}. \quad . \quad (11)$$

The value of A is a maximum for a value of C given by

$$C=\frac{L}{p^2L^2+R^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (12$$

a value independent of ρ. For this condition of resonance we have

$$A=\frac{E}{R\sqrt{\frac{C}{L}}+\frac{1}{\rho}\sqrt{\frac{L}{C}}}. \quad . \quad . \quad . \quad . \quad (13)$$

Moreover, for a given value of p the particular amplitude obtained at resonance will depend on the relation of the circuit constants. When ρ is infinite the value of A increases steadily with increase of the ratio $\frac{L}{C}$, but when ρ is finite this is not so. For this case, to get maximum amplitude we must have

$$\frac{L}{C} = R\rho, \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

a condition mentioned previously *.

The result demonstrated above may be summarized by saying that if by resonance obtained by capacity variation we mean that the voltage across the circuit condenser, and not the current in the coil, is a maximum, the value of the capacity necessary for resonance is independent of the leak resistance ρ †. Thus any alteration of capacity necessary to restore such voltage resonance when a leaky dielectric is introduced between the plates of the condenser C must be attributed to the effective dielectric constant of the dielectric and not to its conductivity.

4. *Experimental Results.*

The first series of experiments on the dielectric constant of ionized air were carried out by Captain A. G. D. West and one of the writers at Cambridge during 1922-3. In these experiments alternating electromotive forces of frequencies varying from 10^5 to 10^6 cycles per second were used. In one form of apparatus used the experimental condenser consisted of two tin-foil sheets, pasted opposite each other on the walls of a discharge tube of simple type. The discharge was produced either by means of a cold cathode and a 4000 volt Eversheb-Vignolles generator, or by means of a hot cathode (incandescent oxide-coated platinum) and a battery

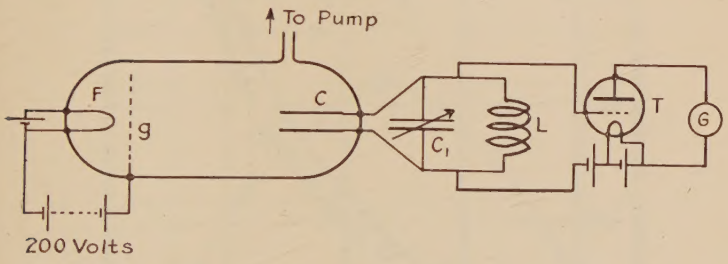
* Appleton, Phil. Mag. xxxvii. p. 129 (1919).

† This result was communicated to Dr. D. Dye in 1927, who informed us that this property of an oscillatory circuit was well known at the National Physical Laboratory. More recently Mr. Albert Campbell has brought to our notice the interesting fact that, when the exciting electromotive force is applied to the oscillatory circuit between points A and B (see fig. 2), and not *via* the coil, one must use current resonance and not voltage resonance to make the appropriate value of the capacity independent of the leak. See Orlich, 'Kapazität und Induktivität,' 1909, p. 120; Jezewski, *Zeit. für Phys.* Bd. xlviii. p. 123 (1928); Doborzynski, *Zeit. für Hochfrequenz*, Bd. xxxi. p. 15 (1928); Lattey and Gatty, Phil. Mag. [7] ii. p. 985 (1929).

of cells. By means of a saturated diode in the circuit the amount of current passing through the diode, and thus through the discharge-tube, could be varied if necessary.

In another form of apparatus the experimental condenser was not situated midway between the anode and cathode, but was arranged as illustrated in fig. 3. Here the tube-current was varied by varying the current through the filament F. The grid G acted as anode and, because of its perforations, permitted the discharge to fill the tube. The experimental condenser C was connected in parallel with a variable calibrated condenser C_1 connected to a coil L. The oscillatory potential across C_1 and C was measured by means of a triode voltmeter T. The galvanometer used in this voltmeter was very sensitive, so that the triode generator supplying the impressed electromotive force could be used some metres away.

Fig. 3.



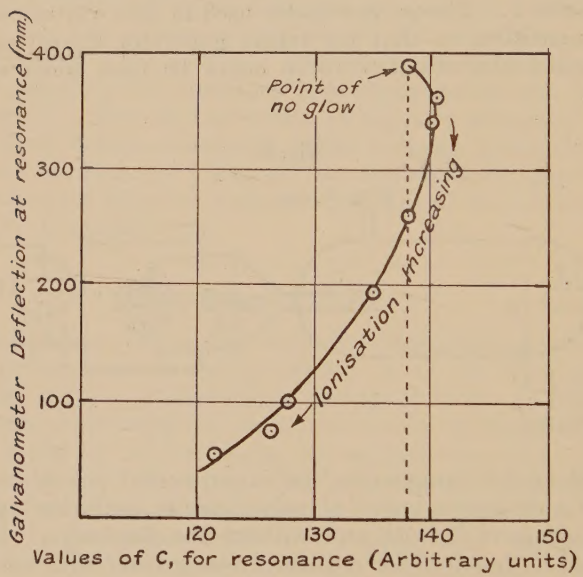
With such arrangements the experimental procedure was to plot a resonance curve of galvanometer deflexion against the readings of C_1 with and without the discharge. If the value of C_1 required for resonance was greater with the discharge than without a diminution of the dielectric constant was indicated. Very often a check on the theory outlined above was obtained by replacing a leak of extremely high resistance, connected across C_1, by one of similar pattern but of sufficiently low resistance to bring about the same damping as that produced by the glow discharge.

For the majority of combinations of tube-current and pressure the apparent dielectric constant was found to be greater than one. Only for the particular conditions of very low pressure and very small tube-current was the diminution of the dielectric constant below unity obtained. This result is illustrated in fig. 4, in which the value of the resonance amplitude is plotted against the value of C_1 to give resonance.

To obtain these figures the value of the ionization current through the tube was steadily increased from a very low value.

From fig. 4 it will be seen that, as the ionization was increased, the effective dielectric constant at first became steadily less than unity, but reached a minimum value, and on increasing finally became greater than unity. It is interesting to note that the galvanometer deflexion at resonance steadily decreases as the ionization increases.

Fig. 4.



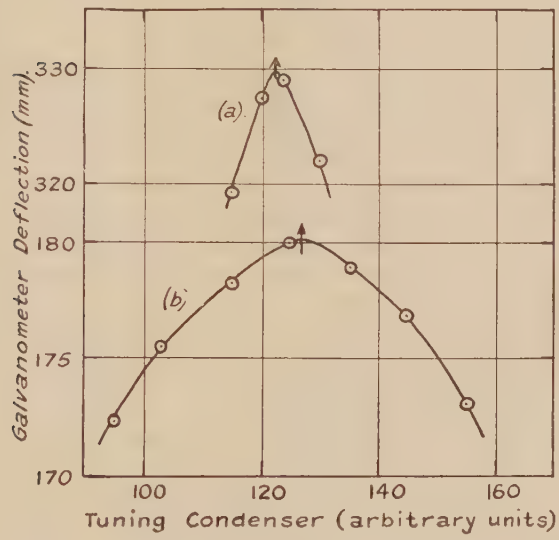
This is characteristic of all similar curves which we have obtained subsequently. In fig. 5 are shown resonance curves with and without the glow. The curve (*a*) shows the relation between galvanometer deflexion and tuning capacity with unionized air between the plates of the experimental condenser. The curve (*b*), taken with the glow present, shows much greater damping and a shift illustrating a dielectric constant less than unity.

The results described above were obtained at pressures of 0·01 to 0·06 mm. of mercury, and they were obtained only for conditions under which the discharge was somewhat difficult to maintain. In all runs carried out at high pressures

evidence of an increase of dielectric constant was always found. It was clear therefore that since, according to the theory outlined above, the dielectric constant of the ionized medium must be less than unity at all pressures and for all values of N, the apparent increase of dielectric constant, found experimentally, must most probably be a spurious effect of the discharge-tube.

Before passing to the second series of experiments carried out at King's College, London, in which the nature of this spurious influence was found, it may be of interest to note

Fig. 5.



that in the experiments carried out by Barton and Kilby in 1913 the criterion of resonance was maximum voltage amplitude across the oscillating circuit, as measured by an electrometer. Although Barton and Kilby applied a theory of free vibration to their results, it seems clear that the theory of forced vibration given above should more properly apply. The shift of Barton and Kilby's cymometer scale should therefore correspond to the readings of C_1 in fig. 4. An examination of Barton and Kilby's paper in the light of this interpretation reveals the fact that their results, if plotted as in fig. 4, would give a curve very similar to that actually shown here. It therefore seems to us probable that Barton and Kilby, in their original experimental work on this

subject, obtained evidence of a dielectric constant less than unity.

The second series of experiments, begun at King's College in 1926, was carried out with the aim of elucidating the phenomenon, experienced in the earlier measurements, of an apparent increase in the capacity of the experimental condenser when dense ionization was introduced, whereas theoretical considerations predicted a decrease. It was also considered desirable to extend the observations on the dielectric constant and absorption of ionized air to cases in which a steady magnetic field was applied, since it had been pointed out* that, if the effective electrical carriers in the atmospheric ionized layer were of electronic mass, the earth's magnetic field would have an influence on the phase velocity and absorption of waves passing through it.

In the first experimental tube used the source of ionization was a cold cathode electric discharge in air at low pressure. The length of the tube was 40 cm., the diameter was 7 cm., and that of both the anode and cathode 3 cm. Midway between these electrodes were sealed four subsidiary electrodes as in fig. 6, the tube having been designed originally for an experiment requiring a rotating electric field. In using the tube for observations on the dielectric constant of ionized gas these plates were connected, so that adjacent pairs formed the two plates of the experimental condenser, which, together with a tuning coil and a finely-adjustable variable condenser, formed an oscillatory circuit, in which forced vibrations were produced by a local valve generator. The discharge was maintained by means of a 6000 volt Evershed-Vignolles motor-generator, the discharge current being maintained constant by the inclusion of a saturated diode in the discharge circuit. The amplitude of the forced vibrations produced in the oscillatory circuit was measured by means of a Cambridge Thermionic Voltmeter.

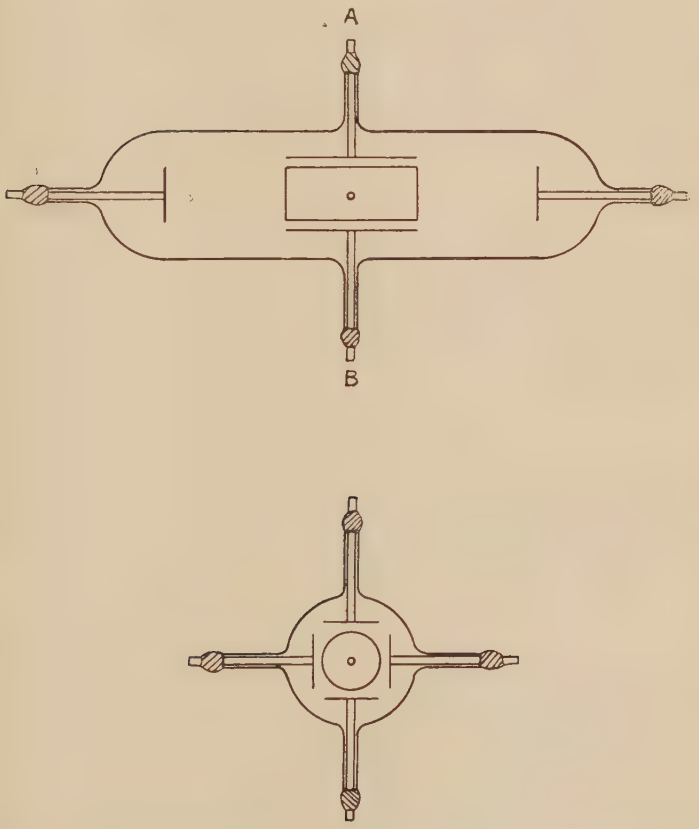
It was realized very early in the course of these experiments that a possible cause of the apparent increase of dielectric constant for cases of intense ionization was the formation of positive ion sheaths on the plates of the experimental condenser. Such sheaths had been recently investigated by Langmuir and Mott-Smith †, and may briefly be described as follows :—When a subsidiary electrode is inserted in a gas discharge it becomes surrounded by a sheath of positive ions or electrons, according to whether it

* Proc. Phys. Soc. xxxvii. part 2, p. 21 D (Feb. 15th, 1925).

† 'General Electric Review,' xxvii. p. 449 (1924).

is at a negative or positive potential with respect to the space potential at that point. If the electrode is insulated from the rest of the apparatus the total current to it is zero, but it assumes a potential which in general differs from the space potential. The velocity of the positive ions is much lower than that of the electrons, and hence the electrode at

Fig. 6.



first collects more electrons per second than positive ions. This state of affairs causes the electrode to acquire a negative potential, some slow electrons consequently failing, from lack of energy, to be collected. Finally, a state of equilibrium is reached, when the positive ion current and the current due to the fastest electrons become equal, the electrode potential reaching a constant value. The acquired negative potential,

as stated above, produces a positive ion sheath around the electrode, and its thickness may be calculated from space-charge equations *.

The potential fall between an auxiliary electrode and the neighbouring part of the main discharge is localized in a sheath, so that, in a problem such as ours, the effect of the sheath is to cause an increase of the effective capacity of the experimental condenser. In other words, the main body of the discharge can be regarded, when sheaths are present, as a conductor which reduces the effective distance between the condenser plates. To investigate this question quantitatively we assume, with Langmuir and Mott-Smith, the space-charge equation for the positive ion current in a sheath, namely

$$i_+ = \frac{AV^{3/2}}{x^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

i_+ being the positive ion current, V the potential fall across the sheath of thickness x, and A a constant involving the ratio of the charge to the mass of the carrier and the area of the electrodes. Allowing for the effect of the space-charge, each sheath will form a condenser of capacity per unit area C′ where

$$C' = \frac{K}{3\pi x}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

In this expression K is the effective dielectric constant of the sheath. If we consider the general body of the discharge as joining in series the two condensers formed by the sheath, we have for the combined capacity per unit area

$$C'' = \frac{K}{6\pi x}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The change of capacity per unit area, due to the introduction of ionization, is $C'' - C$, where C is the capacity between the plates, separated by distance D, before the gas is ionized.

* It should be mentioned here that, as Wilson and Gold (Phil. Mag. [6] xi. p. 484, 1906) have shown in their work on the high-frequency properties of flames, the difference in the mobilities of positive and negative ions gives rise to the formation of ionic sheaths near the electrodes when an oscillatory potential is applied. Ionic sheaths of this type, however, would cause variations of apparent capacity of the experimental condenser which would be dependent on the amplitude of the applied oscillatory potential. No variations of apparent capacity with voltage were found in our experiments, so that we conclude that the effect of this type of sheath, although possibly present, has been masked by the effect of sheaths of the Langmuir type.

$C''-C$ is the quantity which is measured experimentally. If x is small compared with D, $C''-C$ is equal to $\frac{K}{6\pi x}$.

The validity of (17) was verified by finding the change in the effective capacity of the experimental condenser when the potential fall across the sheath was varied. In the case under consideration (*i.e.*, with plane collectors), if we neglect "edge effects" the ions cannot move in orbits which do not intersect the collector, so that the positive ion current is determined solely by the rate at which ions cross the boundary between the sheath and the main discharge. It is therefore independent of the potential of the condenser plates, and remains constant provided the conditions in the tube remain unaltered. We may write (15) as

$$x^2 \propto V^{3/2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

so that using (17)

$$C'' = V^{-3/4} \times \text{const.},$$

or

$$\log C'' = \text{const.} - \tfrac{3}{4} \log V. \quad . \quad . \quad . \quad . \quad (19)$$

Since the value of C'' is usually large compared with the original capacity of the experimental condenser, in the absence of ionization, it is clear that the reduction in the value of the subsidiary condenser of the oscillatory circuit necessary to restore resonance after the discharge is started is a measure of C''.

The relation (19) was tested by means of the tube shown in fig. 6 with a circuit arrangement as shown in fig. 7, where the assembly is as described above except that a potentiometer is included for varying the mean potential of the condenser relative to the anode. The potential difference between the condenser and the anode was read on the voltmeter V. The amplitude of oscillation was measured by means of the thermionic voltmeter T, the circuit L_1C_1 being brought to resonance by varying C_1. The change of C_1 required to restore resonance was a measure of C''.

In fig. 8 is shown the relation obtained experimentally between C'' and V. It will be observed that the points lie, within the limits of experimental error, on a straight line, of slope $-\frac{3}{4}$, as (19) would suggest. It should, of course, be stated that V does not measure the potential between the electrode and the discharge in that region, but the space potential in the discharge was only about -7 volts with respect to the anode, as found by Langmuir's method, and this correction was applied to V in order to obtain fig. 8.

Fig. 7.

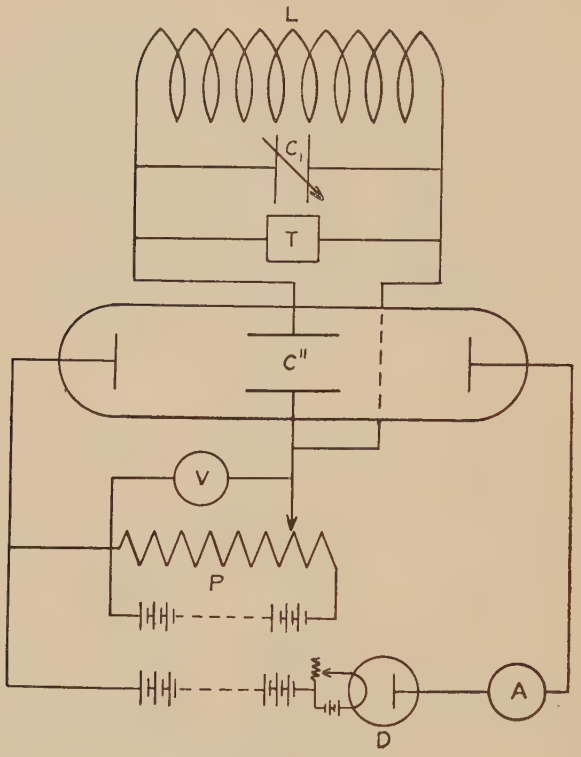
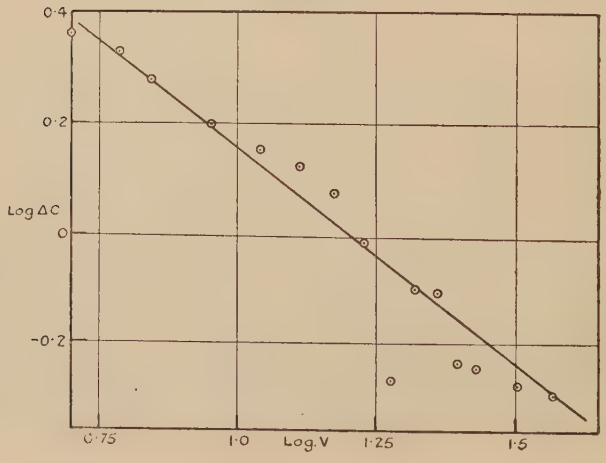


Fig. 8.



In order to examine the behaviour of the condenser when both the effects mentioned above are operative, equations (8), (15), and (17) may be combined. The positive ion current, i, of (15) is proportional to the ion density, N, in the discharge ; hence (15) may be rewritten

$$N \propto \frac{1}{x^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

provided that V is constant. The value of x obtained, when substituted in (17), and using the value of K from (8), yields

$$C'' \propto \left(1 - \frac{4\pi N e^2 m}{m^2 p^2 + g^2}\right) N^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad (21)$$

An examination of the behaviour of (21) reveals that $C'' = 0$ when $N = 0$, whereas experimentally, of course, $C'' = C$, the original capacity of the condenser. The explanation of this is to be found in (20), according to which $x = \infty$ when $N = 0$, regardless of the fact that the experimental tube is of limited dimensions ; the value of x having, in fact, an upper limit of $D/2$, where D is the distance between the condenser plates. Let N' be the ionic density corresponding to $x = D/2$ in (20). Then, for all values of N between 0 and N' the sheath occupies the whole of the dielectric space, and the variations of capacity depend only on the dielectric constant as given by (8) ; in other words, between $N = 0$ and $N = N'$ the capacity of the condenser steadily decreases. For $N = N'$ the sheaths can form according to (20), and the expression (21) is now valid for the capacity C''. It is easily seen that this function increases rapidly at first, with increase of N, then reaches a maximum, and finally assumes negative values. Thus we see that, as the ionization is increased, the value of C'' should at first fall, and then, at the critical value of N, should start to increase. For further increase of N it should reach a maximum, and then should steadily fall.

With the wave-length first used (about 300 m.) no diminution of capacity was observed. A calculation of the amplitude of vibration of the ions in the tube, assuming a friction coefficient of $\frac{m}{\tau}$ (τ = time between collision of ions), revealed that this was comparable with the dimensions of the tube, and consequently ions suffered interference by collisions with the condenser plates and the walls of the tube. This indicated that a much higher frequency was necessary for the success of the experiment.

For work with lower pressures and higher frequencies a new experimental arrangement was used, with which the effect of an imposed magnetic field could also be studied. The cathode of the tube was a tungsten filament taking a current of 2 amps, the anode being an aluminium disk 2 cm. in diameter situated about 12 cm. from the cathode. Between these were sealed two condenser plates, 5 cm. long and 2 cm. wide, separated by a distance of 2 cm. The long sides were parallel with the axis of the discharge-tube, which was about 5 cm. in diameter.

The tube A of fig. 9 was mounted in a vertical position, and the condenser plates were connected to the ends of a pair of parallel brass rods 216 cm. in length, which, with a short-circuiting bar, constituted a Lecher wire system suitable for a wave-length of about 5 m. The amplitude of oscillation was measured in arbitrary units by means of a triode detector, T, coupled to the ends of the Lecher wires by two small condensers, CC, consisting of short brass tubes, which were insulated from the rods by thin mica. The steady current through the galvanometer, G, was balanced out by that from a single cell controlled by a high variable resistance, R. On tuning this circuit, it was found that the short-circuiting bar B was approximately at the mid-point of the Lecher wires, and thus the pick-up could be taken from the ends CC, which was very convenient. In order to be sure that it was the part BA, and not BC, that was in resonance with the oscillator, the condenser plates were disconnected at A, and the expected detuning effect was observed.

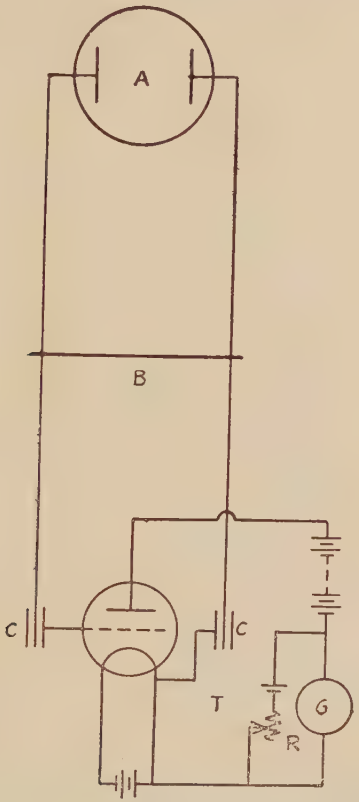
A pair of Helmholtz coils was mounted concentrically with the tube, so that a uniform magnetic field could be applied parallel to the condenser plates. The disposition of these coils relative to the tube is shown in fig. 10.

A triode generator of waves 5·46 metres in length was used to induce oscillations in the Lecher wire system. In the experiments without an applied magnetic field the relation between the ionization and the tuning of the Lecher wire system was studied. The ionic density was increased by raising the temperature of the filament of the diode in the discharge circuit, thus causing an increase of current through the tube. An attempt was made to measure the ion density in the discharge by means of plotting current-potential characteristics for the condenser plates, as described by Langmuir *. The attempt failed because the negative potential

* *Loc. cit.*

necessary to obtain the straight positive ion current part of the curve was so large that the discharge was very badly distorted long before this condition was reached, the plates showing a tendency to become the cathode. In the absence of any knowledge of the positive ion current, the corrected

Fig. 9.



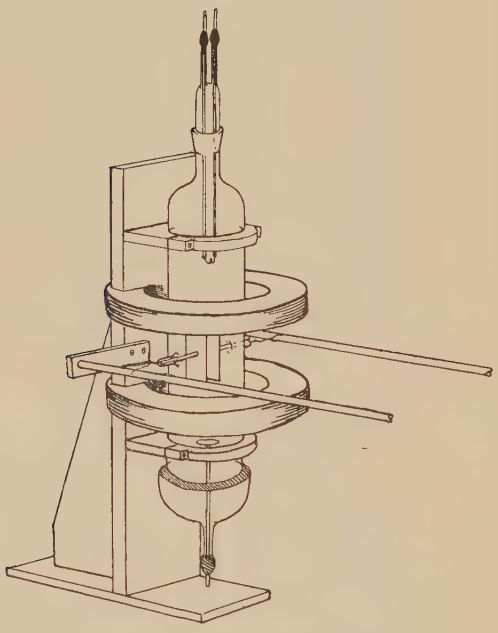
electron current at any part of the curve could not be ascertained ; hence neither the space potential nor the ion density were calculable. It was noticed that, at the pressures used, the discharge was not striated, the negative glow just filling the space between the condenser plates. This is an important point, as it had been observed in previous experiments that spurious results may be obtained owing to the

striations moving along the tube as the pressure or discharge current is varied.

The experimental curve shown in fig. 11 shows the change of position of the short-circuiting bar of the Lecher wire system plotted against the current passing through the discharge-tube, the former being approximately proportional to the change of capacity of the condenser.

The experimental curve (fig. 11) shows very definitely

Fig. 10.

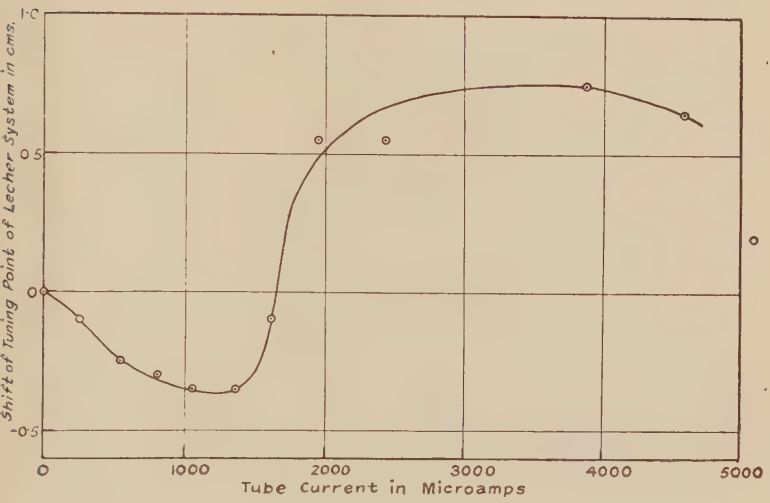


that for small ionization densities the dielectric constant of the gas is less than unity, but that, as the ionization is increased, the apparent dielectric constant increases and becomes greater than unity. Our previous experiments enable us to explain this result as being due to the combined action of the true reduction in the dielectric constant and the formation of ionic sheaths round the electrodes. For very low ionization densities such sheaths do not form, so that the effect sought is not masked. At high densities the formation

of the sheaths increases the apparent capacity of the system, and the effective dielectric constant is found to be greater than unity.

An examination of (21) leads us to the conclusion that when N becomes very large C″ ultimately approaches zero and then assumes negative values, in which case it is equivalent to a self-inductance. This effect was not observed in practice, owing to instability of the discharge for large values of N, but fig. 11 shows that there is evidence at least of a maximum value of C″.

Fig. 11.



5. *Experimental Results (continued).*

The Influence of an Imposed Magnetic Field.

As mentioned above, particular interest in connexion with theories of wireless propagation centres round the question as to whether the electrical carriers in ionized gas are negative particles of electronic mass or ions of molecular mass. The particular point can, perhaps, best be seen by comparing the equations for the refractive index μ of ionized gas for wireless waves with and without an applied magnetic field. We consider, for simplicity, collisional friction suffered by the electrical carriers to be negligible, and consider a case of propagation along the lines of magnetic force. For the

case of no imposed magnetic field and small ionization, we have

$$\mu^2 = 1 - \frac{4\pi N e^2/m}{p^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

For the case of propagation along a magnetic field of strength H_0 we have

$$\mu^2 = 1 - \frac{4\pi N e^2/m}{p^2 \pm p p_0}, \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where

$$p_0 = \frac{H_0 e}{mc} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

If the electrical carriers are electrons the upper and lower signs in (23) refer to the left-handed and right-handed circularly polarized components which travel along the lines of magnetic force. For one of these components there is a kind of resonance when p is equal to p_0, which is the angular frequency with which free electrons spiral round the lines of force. The value of the critical frequency evidently depends on H_0 and m. For the earth's field of 0·5 gauss and carriers of electronic mass it is $1{\cdot}4 \times 10^6$ cycles per second, a frequency well within the wireless spectrum, while for the same field and molecules of, say, nitrogen, which gas probably predominated in the discharge-tube, it is 28 cycles per second.

The experiments to be described were carried out with the idea of establishing whether or not this magneto-ionic resonance existed. At first experiments were made using a discharge-tube oriented along the lines of total force of the earth, but these were unsuccessful as the tube was constructed with a cold cathode, and it was impossible with it to maintain a discharge current small enough and with pressures low enough to prevent the formation of sheaths round the electrodes.

In designing a new tube with a hot cathode it was felt that, for a number of reasons, a better way of testing the theory would be to use an imposed magnetic field which would be much stronger than that due to the discharge current itself. This necessitated the use of very high frequencies (of the order of 10^8 cycles per second) in order to test for resonance phenomena due to the gyric motion of electrons. As has been shown above, the necessity of preventing the formation of sheaths also required small ionization densities.

The experimental assembly has been already shown in fig. 9. The magnetic field was applied in the direction of

the discharge current, and its effect on the absorption in the experimental condenser studied To do this the variation of the amplitude of the forced oscillations maintained in the Lecher wire system was noted as the current through the Helmholtz coils was increased. Three different wave-lengths were used and in each case it was found that at one particular value of the magnetic field a pronounced absorption took place.

Before describing the results further it is, however, necessary to examine more closely the relation of the experimental conditions to those contemplated in wave propagation theories. In our experiments the electric forces acting on the electrons made them vibrate at right angles to the direction of the magnetic field, and we consider that this state of affairs is comparable with the case examined by Lorentz * for propagation of waves at right angles to an imposed magnetic field, the electric vector being also at right angles to the field. In such a case, as Lorentz points out, the formulæ for the phase velocity and absorption coefficient of the waves become so complicated as to be intractable except in special cases, which, fortunately, are the only ones arising in practice. The same remarks will obviously apply equally to the formulæ for dielectric constant and conductivity of the gas for applied electromotive forces of the same frequency as that of the waves. We consider here the special conditions which seem applicable to our problem, and assume that the number of collisions per second (f) between an electron and gas molecules is small compared with p. Remembering that, although the electric displacement in a direction perpendicular both to the magnetic field and the alternating electric forces is zero, there is a definite polarization, and therefore a field in that direction, we may deduce that the conductivity of the gas (σ) is given by

$$\sigma = \frac{p\beta\{(4\pi-\alpha)^2+\gamma^2\}}{\{\alpha^2-4\pi\alpha-\gamma^2\}^2}, \quad . \quad . \quad . \quad . \quad (25)$$

where $\alpha = \frac{mp^2}{Ne^2} + \frac{4\pi}{3}$, $\beta = \frac{mpf}{Ne^2}$, and $\gamma = \frac{mpp_0}{Ne^2}$ †.

By using a small ionization it is possible to reduce N so that α is large compared with unity, in which case (24) becomes

$$\sigma = \frac{p\beta(\alpha^2+\gamma^2)}{(\alpha^2-\gamma^2)^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

* 'Theory of Electrons,' p. 160 (Leipsig, 1916).

† The notation is here slightly different from that used by Lorentz.

or

$$\sigma = \frac{Ne^2 f(p^2+p_0^2)}{m(p^2-p_0^2)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

The value of σ is therefore a maximum when

$$p = p_0 = \frac{H_0 e}{mc}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

We thus see that in the case in which the ionization is small we should expect the critical value of the magnetic field producing maximum absorption to be proportional to the excitation frequency, and to be given by (28), but, if the ionization is appreciable, the relation is not so simple.

Fig. 12.

For a wave-length of 5·46 metres (corresponding to an angular frequency $p = 3{\cdot}45 \times 10^8$ cycles per second) the relation between the potential amplitude produced in the Lecher wire system and the current through the Helmholtz coils was as exhibited in fig. 12, where a pronounced absorption is noted for a current of 0·78 ampere, which corresponds to a magnetic field of 20·5 gauss.

It will be seen that other variations take place, but the maxima and minima are not marked and they are not sharp. They may be due to imperfect screening of the Lecher wire system from the observer, it being a matter of difficulty to ensure that the capacity to the observer is exactly the same after each adjustment of the magnetic field current.

Experiments were made with two other wave-lengths which yielded similar results. In the following Table are shown the frequencies used, the critical values of H_0 producing

maximum absorption, and also the critical value of H_0 calculated from (28) :—

Angular frequency (cycles per sec.).	Critical Field (gauss). Exp. observed.	Critical Field (gauss). Calc. from (28).
$2{\cdot}96 \times 10^8$	16·5	16·7
$3{\cdot}45 \times 10^8$	20·5	19·4
$5{\cdot}48 \times 10^8$	31·5	31·0

In all three cases it will be seen that the observed values of H_0 are not very different from the calculated values, so that we conclude that the effective electrical carriers in the ionized air are electrons.

In a recent note Benner * has demonstrated the quasi-resonance phenomena of free electrons in a magnetic field. Benner used a wireless vacuum valve, the electrons being emitted by a hot filament in the usual way. As the tube used was a transmitting valve, and therefore one of extreme exhaustion, the conditions are different from those in our experiments, where the problem was to find the nature of the electrical carriers in ionized gas at low pressures. It is of interest to note that complete agreement between the calculated and observed values of the critical value of H_0 was not observed by Benner, his observed values being 1.2 per cent. higher than the theoretical value. This may be due to the fact that the wireless valve used most probably had an anode of nickel, which, being magnetic, would effectively reduce the imposed field.

6. *Summary.*

The experiments described above confirm earlier work on the subject of the dielectric constant of ionized gases for radio-frequency electromotive forces, in that a dielectric constant less than unity has been observed under certain conditions. This result was obtained only with very low ionization densities and low pressures. The existence of an apparent dielectric constant greater than unity at higher ionization densities, which appears to have been observed by all workers on the subject, has been the subject of special study, and has been shown to be due to the formation of ionic sheaths round the experimental electrodes, which effectively increase the capacity of the experimental condenser, and so

* *Loc. cit.*

mask the true effect sought. The variation in the thickness of these sheaths with the potential across them has been examined by a wireless method, the result being in agreement with the theory of collectors developed by Langmuir and Mott-Smith.

The influence of an imposed magnetic field on the radio-frequency properities of ionized air has been studied, and the existence of an Inverse Zeeman effect for free electrons demonstrated. This effect was predicted in connexion with the magneto-ionic theory * of the atmospheric deviation of wireless waves. For a particular value of the imposed magnetic field a critical frequency is found for which pronounced absorption occurs. The relative magnitudes of the imposed magnetic field and the critical frequency yield a value of $\frac{e}{m}$ of $1{\cdot}74 \times 10^7$ e.m.u. for the electric carriers, so that there is therefore no doubt that they are electrons.

The experiments therefore support the theory of Sir Joseph Larmor, according to which the refractive deviation of wireless waves in the upper atmosphere is due to the influence of free electrons.

7. *Acknowledgment.*

In conclusion, we wish to express our thanks to Captain A. G. D. West for his assistance in the earlier series of these experiments, which were carried out as part of the programme of the Radio Research Board of the Department of Scientific and Industrial Research.

XCI. *The Values and Inter-relationships of c, e, h, M_p, m_o, G, and R.* *By* W. N. Bond, *M.A., D.Sc., F.Inst.P., Lecturer in Physics in the University of Reading* †.

Introduction.

OF the universal constants with which we are concerned in Physics, probably the most important are :—

c, the velocity of light;

e, the electronic (or protonic) charge;

h, Planck's constant;

* See Proc. Phys. Soc. xxxvii. part 2, p. 21 D (Feb. 15th, 1925).

† Communicated by the Author.

M_p, and m_o, the masses of proton and electron ; and

G, the gravitational constant.

With suitable definitions these have all been measured in terms of our three primary units of mass, length, and time, and hence their dimensions are expressible in terms of [M], [L], and [T]. It is well known that for six quantities, expressible in terms of three primary units, there are (in general) three independent non-dimensional products, the numerical values of which will be independent of the size of our primary units. In the present instance three independent products are found, such as

$$hc/e^2,\ M_p/m_o,\ \text{and}\ hc/M_p{}^2G. \quad . \quad . \quad . \quad . \quad (1)$$

These products are rather simpler in form than if the six quantities had been any six physical quantities chosen at random. Moreover, the numerical values of the first two (860 and 1840 approximately) are nearer in magnitude to unity than might be expected by chance (where the individual quantities range numerically from 3×10^{10} to 9×10^{-28}). Hence we might expect the first two products to have physical significance. It might at first be thought that the third non-dimensional product was certainly not of significance, as its numerical value is about 10^{39}. But, on the other hand, it must be borne in mind that we continue to have evidence of the inter-relatedness of natural phenomena, and that it is unlikely that G should form an exception.

Apart from experimental measurement, various suggestions have been made as to the values of these non-dimensional products. Thus Lewis and Adams * suggested

$$\frac{hc}{2\pi e^2} = 8\pi\left(\frac{8\pi^5}{15}\right)^{1/3} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and Eddington †

$$\frac{hc}{2\pi e^2} = 137. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Perles ‡ suggested

$$\frac{hc}{e^2} = \frac{M_p/m_o}{\pi - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and Fürth §

$$\frac{hc}{e^2} = \frac{15}{32}\frac{(M_p+m_o)^2}{M_p m_o}, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

* Lewis and Adams, Phys. Rev. (2) iii. p. 92 (1914).

† Eddington, 'Nature,' Aug. 24, 1929, p. 320; Proc. Roy. Soc. A, cxxvi. p. 696 (1930).

‡ Perles, *Naturwiss.* xvi. p. 1094 (1928).

§ Fürth, *Phys. Zeit.* xxx. p. 895 (1929).

and

$$\frac{hc}{2(M_p+m_o)^2G}=\frac{\pi}{2}(16)^{32}. \quad . \quad . \quad . \quad (6)$$

It is the purpose of this paper to discuss the evidence supporting any of these suggestions or theories. It is concluded that two, and possibly three, relationships are significant; and incidentally the numerical values here suggested for the six universal constants differ slightly from those recently given * (with the exception of the value of the velocity of light).

The Values of c, e, h, hc/e^2 and e/m.

The value of c we may consider known to a very high degree of accuracy (Birge, *loc. cit.*). The values Birge attributes to h and hc/e^2 are chiefly in doubt owing to the uncertainty of the value to be assumed for e. Before discussing the values obtained experimentally for e, we will consider another method of estimating e and h.

In any method of measuring h, experiments are performed resulting in the estimate of a number, A, that occurs in an equation of the form

$$h=Ae^n, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where n has values 1, $1\frac{1}{3}$, $1\frac{2}{3}$, according to the method used. If a second method were used involving a different power of e, we should have, similarly,

$$h=A'e^{n'}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7^*)$$

Apart from errors of experiment or theory, these two equations would together yield values of e and h. To minimise the effects of errors, all the accurate experiments should be used, and not only a pair as described above.

To illustrate the calculation I show in the figure the values of h collected by Birge (*loc. cit.*) plotted against the values of the index n to which e occurs in the estimation of h. All the values here plotted are based on the assumed value (Birge) of

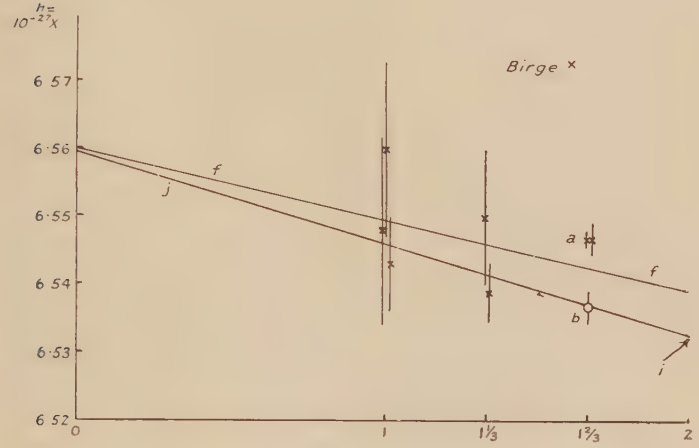
$$e=(4{\cdot}770\pm0{\cdot}005)\times10^{-10}\text{ abs-es-unit.}$$

If this value of e be correct, the values of h deduced from experiment should not vary systematically with the index n. On the other hand, if this assumed value of e be too small by a small percentage E, the deduced values of h will also be on this account too small, and by an amount very nearly equal

* Birge, Phys. Rev. Supp. i. No. 1, pp. 1–73 (July 1929).

to nE per cent. In other words, the straight line best fitting the points in the figure would not be horizontal but inclined, intersecting the h-axis nearly at the true value of h, and having an ordinate where $n = 1$ of about E per cent. less.

Before finding the best straight line to fit these values, a digression will be made. A noticeable feature of Prof. Birge's paper is that he attributes to e/m two values—the "spectroscopic" and the "deflexion." He decides that the values of e/m estimated from a comparison of the Hydrogen and Helium spectra, and from the Zeeman effect, agree very closely, but differ (for some unexplained reason) from the value deduced from deflexion experiments by more than can



Values of the power n to which e is raised in deducing h.

be accounted for by experimental errors. Now the method of estimating h by means of Rydberg's constant necessitates a knowledge of e/m. Prof. Birge in this case makes use of the "spectroscopic" value of e/m (a in figure). As there is no definite evidence requiring the rejection of the "deflexion" value, I have at first used *three* estimates of h, those based on the two spectroscopic methods being at a and that based on the deflexion value of e/m at b (see figure).

In proceeding to find the straight line that best fits the points in the figure, account might be taken of the estimated probable errors of the different points. These errors are, however, only estimates, and I feel that it is more satisfactory at first to attribute equal weight to each of the points in the

diagram. Doing this, and using the ordinary method of least squares, I obtain the values (*ff* in figure) :—

$$\left.\begin{aligned} e &= (4{\cdot}777_4 \pm 0{\cdot}003_9) \times 10^{-10} \text{ abs-es-unit,} \\ h &= (6{\cdot}560 \pm 0{\cdot}007) \times 10^{-27} \text{ erg . sec.,} \end{aligned}\right\} \quad \ldots (8)$$

which do not depend on any direct determination of e.

Together with the value of c given by Birge, and using his method of estimating the probable error, we then obtain

$$ch/2\pi e^2 = 137{\cdot}14 \pm 0{\cdot}11.$$

Before discussing this result, let us consider the results of direct determinations of e (by oil-drop and ruled-grating methods). Birge considers values due to Millikan, Bäcklin and Wadlund (and at the end of his paper mentions an unpublished value due to Bearden). He rejects Bäcklin's value, partly because it does not agree with a calculation involving Rydberg's constant and the "spectroscopic" value of e/m, and also because Bäcklin's pioneer work may contain unsuspected errors.

Considering the results now, I know of no definite reason for rejecting any of the four, even though their estimated probable errors are little more than a half of what would be required to account for the differences between their results. (We may note that Bearden's published results do not appear as abnormal as the values mentioned, before publication, by Birge.) Thus we have :—

Millikan	$4{\cdot}768 \pm 0{\cdot}005$	$\times 10^{-10}$ abs-es-unit.
Bäcklin	$4{\cdot}794 \pm 0{\cdot}006$	
Wadlund	$4{\cdot}775_7 \pm 0{\cdot}0076$	
Bearden	$4{\cdot}809_5$	

As the estimated probable errors are all of the same order, but appear to be underestimates, I take the unweighted mean :

$$\left.\begin{aligned} e &= (4{\cdot}787 \pm 0{\cdot}007) \times 10^{-10} \text{ abs-es-unit.} \end{aligned}\right.$$

Using this estimate of e, but otherwise following Birge as to data and method of calculation, we obtain

$$\left.\begin{aligned} h &= (6{\cdot}576 \pm 0{\cdot}012) \times 10^{-27} \text{ erg . sec.} \end{aligned}\right\} \quad \ldots (9)$$

and

$$hc/2\pi e^2 = 136{\cdot}94 \pm 0{\cdot}15.$$

The estimated values of $hc/2\pi e^2$ given in (8) and (9) may be compared with Birge's estimate of $137{\cdot}29 \pm 0{\cdot}11$. The new estimates are further from the suggestion of Lewis and Adams, 137·348 (equation (2)), but nearer to that of Eddington, 137 (equation (3)). Prof. Birge's estimate differs from 137 by 2·6 times his probable error, which, if due to chance, has only a probability of $\frac{1}{17}$. My less accurate estimate (equation (9)) differs from 137 by only 0·4 times the probable error; and my more accurate (equation (8)) by 1·27 times the probable error.

I conclude, therefore, that the new estimates given above form definite evidence for Professor Sir A. Eddington's suggestion. At this stage I think we may safely *assume* as correct Eddington's equation:

$$\frac{hc}{2\pi e^2} = 137. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(This equation appears to have a much better theoretical basis than that of Lewis and Adams.)

Equation (3) can now be used with the measurements of A of equation (7) to obtain a more accurate estimate of e. This is equivalent to fitting to the points in the figure a straight line through the fixed point i. The probable errors of the points (apart from error in the assumed value of $e = 4{\cdot}770 \times 10^{-10}$) I have deduced from Birge's data, and have indicated by the vertical lines in the figure. It is evident that if the points are to fit on a straight line through i, the point a (based on Rydberg's constant and the "spectroscopic" value * of e/m) must be discarded, but that the point b (based on Rydberg and the "deflexion" value of e/m) may be retained. This is the reverse of Birge's procedure. I then fitted the line (ij in figure) by the usual methods, weighting in accordance with the probable errors of the points. The result shows the errors to have been overestimated, as judged by internal consistency, so I base the estimate of the final probable error on the residuals. Finally,

$$e = (4{\cdot}779_3 \pm 0{\cdot}0017) \times 10^{-10}.$$

Taking the weighted mean of this value and the mean direct estimate of equation (9) I get

$$\left.\begin{aligned} &\underline{e = (4{\cdot}779_7 \pm 0{\cdot}0017) \times 10^{-10} \text{ abs-es-unit,}} \\ &\text{and from equation (3),} \\ &\underline{h = (6{\cdot}559_6 \pm 0{\cdot}0046) \times 10^{-27} \text{ erg . sec.}} \end{aligned}\right\} \quad . \quad . \quad (10)$$

* This value is smaller than *all* the final values given in Geiger and Scheel's 'Handbuch der Physik,' xxii. p. 81.

This value for e could be used together with Rydberg's constant to estimate e/m were it not that the point b (see figure) assumed a value of e/m. The determination of e was therefore repeated, not using point b (nor point a), and this slightly different estimate of e, together with Rydberg's constant, gave

$$e/m = (1{\cdot}7688_0 \pm 0{\cdot}0007_1) \times 10^7 \text{ abs-em-unit} \cdot g^{-1}.$$

This agrees well with Birge's "deflexion" value of

$$1{\cdot}7689 \pm 0{\cdot}0018,$$

but disagrees with his "spectroscopic" value

$$1{\cdot}761 \pm 0{\cdot}001.$$

The disagreement is now not between "deflexion" and "spectroscopic," but between "deflexion" and "Rydberg" on the one hand and methods depending on small spectroscopic *differences* on the other hand. This appears less difficult to account for, and may suggest that the results Birge gives, depending on the spectroscopic *differences* are not quite accurate.

Taking the weighted mean of the "deflexion" and "Rydberg" values we obtain :—

$$e/m = (1{\cdot}7688_2 \pm 0{\cdot}0006_3) \times 10^7 \text{ abs-em-unit} \cdot g^{-1} \quad . \quad (11)$$

This may be compared with the estimate of the International Critical Tables, $1{\cdot}769 \pm 0{\cdot}003$, and with that of the *Handbuch der Physik*, $1{\cdot}766$; from the data given in the latter book I estimate $1{\cdot}767_7 \pm 0{\cdot}001$.

The results of this part of the paper are now contained in equations (3), (10), and (11).

The Value of M_p/m_o.

Using the value of e/m given in equation (11), and following Birge as to other data and as to method of calculation, we obtain directly

$$\left.\begin{aligned} \frac{M_H}{m_o} &= 1847{\cdot}43 \pm 0{\cdot}65, \\ \frac{M_p}{m_o} = \frac{M_H - m_o}{m_o} &= 1846{\cdot}43 \pm 0{\cdot}65, \\ \frac{(M_p + m_o)^2}{M_p m_o} &= 1848{\cdot}43 \pm 0{\cdot}65, \end{aligned}\right\} \quad . \quad . \quad . \quad (12)$$

Testing the suggestions contained in equations (4) and (5) by means of data of (3) and (12), we find that

$$\pi - 1 = 2{\cdot}14159, \quad \frac{M_p/m_o}{hc/e^2} = 2{\cdot}1450 \pm 0{\cdot}0007_5$$

and

$$\frac{32}{15} = 2{\cdot}1333, \quad \frac{(M_p + m_o)^2/M_p m_o}{hc/e^2} = 2{\cdot}1472 \pm 0{\cdot}0007_5.$$

The differences between my estimates and the suggested values are in the two cases 4·5 and 18·5 times the probable errors. Moreover, it is only the latter equation, (5), that has a theoretical basis. Hence neither of the equations (4) and (5) seems tenable.

If the values of equation (12) be divided by 2π, we obtain

$$294{\cdot}02 + 0{\cdot}10,$$
$$293{\cdot}86 \pm 0{\cdot}10,$$
$$294{\cdot}18 \pm 0{\cdot}10,$$

and I should like to suggest that one of these should, perhaps, be exactly 294.

The Values of $\dfrac{hc}{2(M_p + m_o)^2 G}$ *and* G.

Fürth (*loc. cit.*), in putting forward the theoretical suggestion (equation (6)), takes the values of the quantities as given by Birge (*loc. cit.*) and obtains for the two sides of the suggested equality the values

$$(5{\cdot}33 \pm 0{\cdot}03) \times 10^{38} \quad \text{and} \quad 5{\cdot}34 \times 10^{38}.$$

If we assume that we have now enough theoretical and experimental evidence for Eddington's suggestion (equation (3)), we can make a more rigorous test of Fürth's suggestion. Thus equation (6) can be transformed into

$$\frac{hc}{2\pi e^2} = \frac{16^{32}}{2}\left(\frac{H}{Fc}\right)^2 . G,$$

where H denotes the atomic weight (relative to O = 16) of Hydrogen, and F is the Faraday constant. Taking the values of H, F, and c given by Birge, we get

$$137 = \frac{16^{32}}{2}\left\{\frac{1{\cdot}00777 \pm 0{\cdot}00002}{(2{\cdot}8927 \pm 0{\cdot}0002) \times 10^{14}}\right\}^2 G.$$

Hence

$$G = (6{\cdot}635 \pm 0{\cdot}001) \times 10^{-8} \text{ dyne} . \text{cm}^2 . \text{g}^{-2}. \quad . \quad (13)$$

This does not agree at all well with the value Birge (*loc. cit.*) adopts,

$$(6{\cdot}664 \pm 0{\cdot}002) \times 10^{-8},$$

but it is in moderate agreement with the values adopted in Geiger and Scheel's 'Handbuch der Physik' (ii. p. 491),

$$6{\cdot}6_5 \times 10^{-8},$$

and in the 'International Critical Tables' (i. p. 17),

$$(6{\cdot}66 \pm 0{\cdot}01) \times 10^{-8}.$$

As Prof. Birge's final estimate of G is based entirely on the work of Heyl, I undertook a fresh analysis of all the estimates I could find, deducing an *experimental* value

$$\underline{G = (6{\cdot}65 \pm 0{\cdot}01) \times 10^{-8} \text{ dyne} \,.\, \text{cm}^2 \,.\, \text{g}^{-2}.} \quad . \quad . \quad (14)$$

This again is in reasonable agreement with the value given by Fürth's suggestion (equation (13)). I conclude that this agreement is significant, and that Prof. Birge's adoption of a value for G entirely based on the results of one experimenter has resulted in his considerably underestimating the probable error.

We may notice that, according to Fürth's suggestion, an experimental number of the order 10^{39} is expressed in the comparatively simple form of $\pi(16)^{32}$, with an error that appears to be certainly less than $\frac{1}{2}$ per cent., and is probably of the order $\frac{1}{4}$ per cent. or less. This agreement can hardly be considered fortuitous, even if we make allowance for possible choice of variables, etc.

If we accept the evidence for Fürth's suggestion (equation (6)), it then appears that the indirect estimate of G (equation (13)), based on equation (6), is more accurate than the direct estimates such as (14). It is, however, still possible that Fürth's suggested equation might be subject to some small correction term.

The results of this part of the paper are then contained in equations (6), (13), and (14).

Conclusion and the Value of $M_p cR/h$.

I believe that there is sufficient experimental evidence to support the suggested relationships

(Eddington) $$hc/2\pi e^2 = 137, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(Fürth) $$hc/\pi(M_p + m_o)^2 G = (16)^{32}. \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Assuming these, I obtain

$$e = (4{\cdot}779_7 \pm 0{\cdot}0017) \times 10^{-10} \text{ abs-es-unit},$$

$$h = (6{\cdot}559_6 \pm 0{\cdot}0046) \times 10^{-27} \text{ erg} \,.\, \text{sec.},$$

$$e/m = (1{\cdot}7688_2 \pm 0{\cdot}0006_3) \times 10^7 \text{ abs-em-unit} \cdot \text{g}^{-1},$$
$$M_p/m_o = 1846{\cdot}43 \pm 0{\cdot}65,$$
$$G = (6{\cdot}635 \pm 0{\cdot}001) \times 10^{-8} \text{ dyne} \cdot \text{cm}^2 \cdot \text{g}^{-2}.$$

I further suggest that there may be significance in the fact that the values of

$$M_H/2\pi m_o, \quad M_P/2\pi m_o, \quad \text{and} \quad (M_p + m_o)^2/2\pi M_p m_o,$$

are within experimental error of 294.

Finally, we may notice that the universal constant "the radius of curvature of space-time" may also prove to be related to the universal constants considered above.

Thus, taking the estimate given by Silberstein ('Nature,' Aug. 3, 1929, p. 179) of $R = 5{\cdot}74 \times 10^6$ light-years, with an uncertainty of about $2\frac{1}{2}$ per cent., I find

$$M_p cR/h = (0{\cdot}121 \pm 0{\cdot}003) \times (16)^{32},$$

which suggests to me $M_p cR/h = \frac{1}{8}(16)^{32}$.

This may have some bearing on the fact that, according to Weyl (*Annalen der Physik*, lix. p. 129), the radius of curvature of space-time, the electrical radius of the electron, and the gravitational radius of the electron should form approximately a geometric progression.

Department of Physics,
University of Reading,
July 28th, 1930.

XCII. *On the Glow Discharge at the Active Electrode of an Electrolytic Rectifier.* *By* JOHN S. FORREST, *M.A.*, *Mackay-Smith Scholar in the University of Glasgow* *.

[Plate XI.]

1. *Introduction.*

THE mode of action of the electrolytic rectifier has been the subject of many investigations since 1905, but, owing to the large number of variables involved, the problem is a difficult one, and, so far, no satisfactory theory has been propounded. The present paper, however, does not deal primarily with the rectifying action of these cells, but an interesting subsidiary phenomenon is discussed, namely, the luminosity which, under certain conditions, appears on

* Communicated by E. Taylor Jones, D.Sc.

the surface of the active electrode. It is probable that a close study of this luminosity might lead to a more complete theory of the rectifying action of the electrolytic cell. In the following sections an account is given of some experiments which were made in order to find out something about the nature of the luminosity.

2. *Description of the Electrolytic Cells used in the Experiments.*

As has been remarked above, the properties of electrolytic cells are functions of a large number of variables, and therefore a fairly exact description of the cells used will be given. For the purposes of the present investigation only three types of cell were found to be at all suitable, namely, cells with active electrodes of aluminium, tantalum, and tungsten.

In the aluminium cell the active electrode was of commercial sheet aluminium immersed in an electrolyte of ammonium phosphate solution

(124 gm. $(NH_4)_2HPO_4 . 12H_2O$ per litre).

Tantalum foil was used for the active electrode in the tantalum cell, while the electrolyte was dilute sulphuric acid (sp. gr. = 1·2) with some ferrous sulphate added to prevent disintegration of the tantalum [1].

In the tungsten cell a tungsten wire (diam. = 1 mm.) was immersed in dilute sulphuric acid (sp. gr. = 1·2).

The immersed area of the active electrode in all cases was 1–2 sq. cm. Sheet lead (commercial) immersed to about the same area was always used for the inactive electrode.

Asymmetric conductivity (or rectification) does not occur unless the active electrode is "formed." To "form" an electrode it may be connected to the positive terminal of a D.C. supply of suitable voltage until the large current which flows initially has diminished to a very small value owing to the insulating oxide film which forms on the electrode surface. With this oxide film there is associated a gas film, and these two films seem to be responsible for the rectifying effect.

3. *General Observations on the Luminosity.*

If the potential difference across the electrodes (active electrode positive) of one of the formed cells described in

the preceding section be gradually increased, the following phenomena are observed. When the P.D. is about 60 v. a faint uniform glow may be seen on the active electrode surface in a dark room. As the P.D. is further increased, the intensity of the glow increases, and then small random scintillations of a violet colour appear on the electrode in addition to the uniform glow. These small sparks give rise to more violent sparks, until, ultimately, the insulating layer breaks down completely and very large currents pass. In this last stage the sparks are often replaced by "arcs" of a reddish colour; this is well shown with tantalum

Fig. 1.

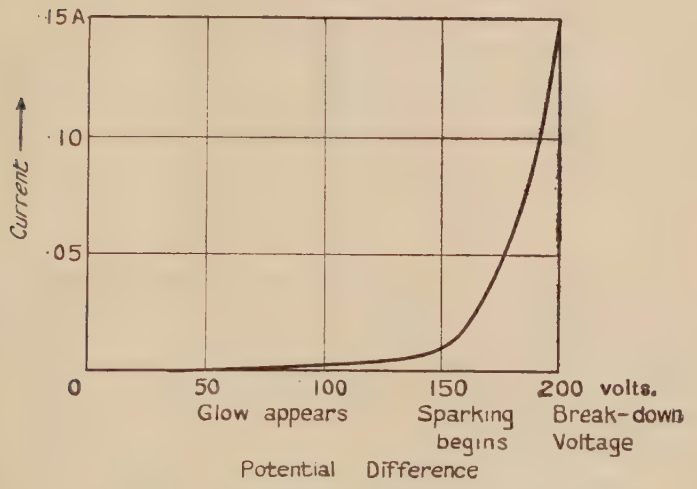


Fig. 1 shows the P.D.-current characteristic for aluminium. For the tantalum and tungsten cells similar curves are obtained, except that the breakdown voltage is about 115 for the tungsten cell and about 90 for the tantalum cell.

The aluminium cell gives the brightest glow, and all subsequent remarks refer to it unless otherwise stated. The tantalum cell gives a faint glow, but it behaves very consistently. The tungsten electrode glows quite brightly, but the insulating layer is rather unstable. It is worth while noting that the oxidation and reduction of the tungsten electrode can be seen easily, as the oxide is white and the reduced metal black.

The glow appears (if the voltage is high enough) and disappears simultaneously with the switching on and off of the current.

If the surface of a glowing electrode is touched with a glass rod, and gentle pressure is applied, bright flashes appear at the point of contact of the rod and the electrode.

Moreover, figures scratched on the surface of a formed electrode shine brightly for some seconds when the electrode is used again.

The glow is usually distributed continuously over the surface of the electrode, but some parts of the electrode, especially at the surface of the electrolyte, may glow more brightly than others. When examined with a microscope ($\times$ 300) the luminosity still appeared to be uniform.

The above experiments strongly suggest that the luminosity is a glow discharge between the metal electrode and the electrolyte, through the layer of gas on the electrode surface. In the following sections the various characteristics of this glow discharge will be described.

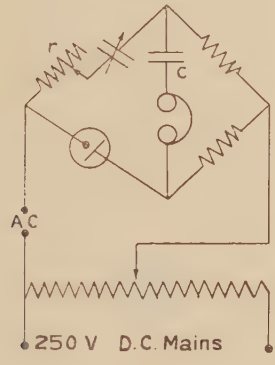
4. *Thickness of the Gas Layer.*

When a P.D. is maintained across a cell, the cell is found to possess a large capacity owing to the active electrode and the electrolyte acting as the plates of a condenser, with the oxide and gas layer for dielectric. The presence of this capacity may be demonstrated by discharging through a galvanometer a cell which has just been disconnected from the current supply; sometimes it is even possible to obtain a small spark on discharge.

In order to measure the capacity in question the bridge shown in fig. 2 was used. This bridge enables the capacity to be measured while a P.D. is maintained across the cell. (Another method of accomplishing the same object has been given by E. M. Dunham [1]). The purpose of condenser C is to safeguard the telephones. The resistance r is used to balance the power factors of the cell and the variable condenser. A source of audio-frequency alternating current is shown at A.C., but the commutator ripple in the mains may be sufficient to work the bridge. By means of this bridge it was found that trustworthy results could be obtained with an ordinary capacity bridge if the measurements were made immediately after the cell was disconnected from the mains.

The laws regarding the capacity of electrolytic cells are fairly well known [2] [3], and need not be repeated here. For the present purpose it is sufficient to state that in these experiments the capacity of the aluminium electrode was about $\cdot 1\mu F/cm.^2$, and that of the tantalum electrode about $\cdot 2\mu F/cm.^2$. These figures correspond to a thickness of the order of 10^{-6} cm. if the dielectric constant is taken to be unity. Now, although the manner in which the oxide and gas layers are associated with each other is not known, it is probably reasonable to take the above figure as the thickness of the *gas* layer. That the oxide layer is at least ten times as thick as the gas layer is indicated by the

Fig. 2.



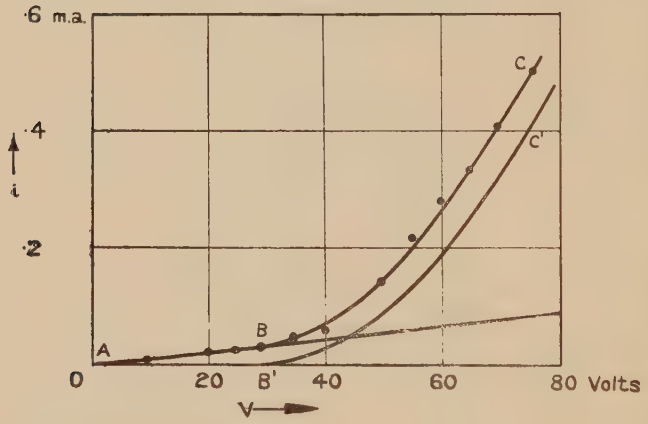
interference colours seen on formed electrodes. Tantalum electrodes show these colours particularly well. In addition, if a formed and dried aluminium electrode be immersed in mercury the capacity between the electrode and the mercury can usually be measured, and it is found to correspond to a thickness of at least 10^{-5} cm. In the following, therefore, the thickness of the gas layer will be taken to be of the order of 10^{-6} cm.

5. *The Potential Difference-Current Characteristic in Rectifying Cells.*

The general form of the P.D.-current curve has been dealt with in section 3, but a more detailed examination brings out some interesting features. The curve of fig. 1 does not show much evidence of the production of a glow

discharge at about 60 v. If, however, the small currents in the region 0–80 v. be measured with a more sensitive instrument, and the graph redrawn to a larger current scale, then the curve ABC of fig. 3 is obtained. This curve seems to indicate that Ohm's law conduction (leakage) takes place alone up to about 30 v., when ionization by collision begins and the current increases more rapidly. If AB is produced, and the leakage current subtracted from the total current, the ionization current is found. B′ C′ gives the glow discharge current through the

Fig. 3.



gas. Tantalum gives a similar curve, but the leakage currents are smaller. The equation of B′ C′ is found to be

$$V - E = k\sqrt{i}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

where V is the applied P.D. and i the current through the cell.

E = 30–40 v. for both aluminium and tantalum.

k = 3000 approx. for aluminium, and

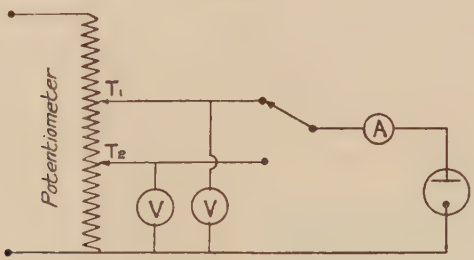
= 10,000 approx. for tantalum in volt ampere units.

The experimental curves agree very closely with equation (A) if certain precautions are taken. The main difficulty is that the thicknesses of the gas and oxide layers vary with the applied voltage. Now, in the present experiments,

it is desirable to keep the thickness of the gas layer constant—the current through the gas and the applied voltage should be the only variables. This leads to the adoption of the arrangement shown in fig. 4. The cell is connected to a fixed tapping T_1 (at 100 v., say) on a potentiometer until a stable state is reached. The voltage (and current) readings in the range 0–80 v. are then obtained by switching over to the variable tapping T_2, and reading the instruments as quickly as possible. Between readings the cell should be connected to T_1. Thus, throughout the experiment the gas layer will be of a nearly constant thickness, namely, the thickness corresponding to 100 v.

At voltages greater than 80 the current increases according to higher powers than the square of the voltage, and it does not appear to be possible to find a simple expression for it which holds over a reasonably large range.

Fig. 4.



6. *Pressure of the Gas.*

In order to obtain an idea of the magnitude of the pressure of the gas in the gas layer a rectifying cell was subjected to external pressures varying from $\frac{1}{40}$ to 4 atmos. Owing to the aqueous electrolyte it was not possible to reduce the pressure (at room temperature) much below 2 cm. of mercury. At this pressure there is very little change in the characteristics of the cell. The scintillations become slightly less violent with the reduction of pressure, but the capacity and breakdown voltage appear to be unaltered. Likewise, when the external pressure was increased to 4 atmos. no change could be detected in the capacity etc. It seems reasonable to suppose, therefore, that the pressure in the gas layer is high, probably amounting to many atmospheres.

7. *The Spectrum of the Glow.*

On account of its faintness the spectrum of the glow is difficult to observe. However, little information is to be gleaned from the spectrum, as it is a continuous one. As the photograph (fig. 6, Pl. XI.) shows it is brightest in the green at about 555 $\mu\mu$. This appears to be the spectrum of oxygen under weak excitation [4]. [The diffuse band in the blue is due to stray light.] The photograph was taken on an Ilford "Golden Iso-zenith" plate (1400 H. & D.), and an exposure of 50 hours was necessary. In order to obtain a brighter glow and shorten the time of exposure as much as possible the cell was supplied with alternating current (see section 10), but the spectrum is the same as that observed visually with direct current.

8. *Influence of Magnetic Fields.*

As the application of a magnetic field sometimes produces large variations in the current flowing through an ordinary discharge-tube, it was thought worth while to try the effect of a magnetic field on an electrolytic cell. Fields up to 4000 gauss, applied both transversely and longitudinally, were used, but the current through the cell and the appearance of the glow were quite unaffected.

9. *Relation between Intensity of Glow and Current.*

Some measurements were made of the intensity of the glow by means of a visual photometer. The results are only roughly accurate, as the intensity of the glow is of the order of ·0001 C.P./cm.^{2}. Such weak intensities are perceived by so-called scotopic vision, and the discriminating power of the scotopic eye is very poor.

An extremely simple form of photometer was used. Outside the cell a comparison surface was supported adjacent to the glowing electrode. The comparison surface was illuminated by a faint green source, while the glowing electrode was screened from this source. The source was set at various distances from the comparison surface, and in each case the current through the cell was adjusted until the electrode and the comparison surface appeared equally bright. The general nature of the results obtained is shown in fig. 5.

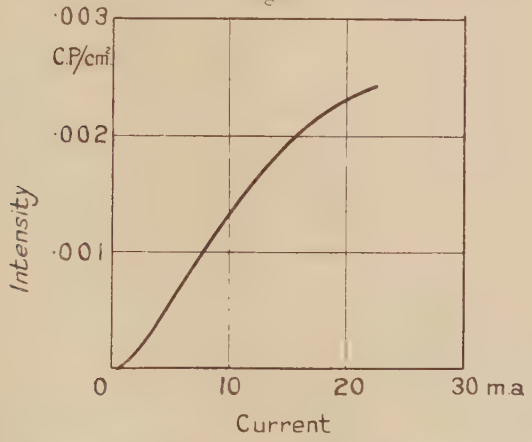
While it is dangerous to draw definite conclusions from results of such a rough character, the following facts seem to emerge :—

(1) The intensity is primarily a function of the current, being over a considerable range approximately proportional to the current.

(2) The curve is, at small values of the current, slightly concave upwards. This may be due to the increase in thickness of the gas layer as the current (and voltage) increase. In this case it was not possible to keep the thickness constant by the method described in section 5, as the readings could not be taken quickly.

(3) A "saturation" value of the intensity seems to be suggested. This may be due to saturation in the usual sense of the term, or it may be due to leakage currents,

Fig. 5.



which become very large as the breakdown voltage is approached.

More satisfactory measurements of the intensity of the glow could probably be made photographically. Fairly long exposures (about 1 hour) would have to be made of the glow for various currents, and the images on the negatives compared with some form of densitometer.

10. *The Cathode Glow.*

In all the above experiments the active electrode was used as the anode, and the resulting glow may be called the "anode glow." If the connexions to a cell which is showing the anode glow are reversed only a momentary glow—the "cathode glow"—is seen, and then the resistance of the cell falls to a low value. This momentary

cathode glow appears even if the cell stands idle for some minutes before the reversed current is applied. Thus, the gas layer persists for some time after the cell is disconnected; capacity measurements (section 4) also demonstrate this fact.

It appears to be impossible, then, to investigate the cathode glow by means of direct current, as the oxide and oxygen layers are speedily reduced when the active electrode is made the cathode. If a cell is supplied with alternating current of suitable voltage and frequency, and if the circuit resistance is not too high, the anode and the cathode glows are produced alternately, and the frequency of the glow is twice the frequency of the alternating current. If the circuit resistance is high the voltage across the cell may be insufficient to produce the cathode glow; the anode glow is then produced alone, and the frequency of the glow is the same as the frequency of the alternating current. The photograph of the spectrum was taken under such conditions, the peak voltages of alternate half-cycles being 180 and 60; the mean current was ·04 amp. and the frequency 25 cycles per second. The greater brightness of the glow on alternating current is probably due to the increased current which flows during the "positive half-cycle" (*i. e.*, the half-cycle which makes the active electrode the anode) after the film has been reduced by the preceding "negative half-cycle."

In order to observe the cathode glow alone it is necessary to view the electrode through a stroboscope disk driven off the alternating current which supplies the rectifier. By means of the stroboscope either the anode or the cathode glow may be examined separately. Moreover, if the slots on one half of the disk are "180° out of phase" with those on the other half, then the anode glow will be seen through one half and the cathode glow through the other. This is a useful arrangement for detecting differences between the anode and cathode glows.

With the help of the stroboscope, it was found that:

(1) the cathode glow becomes visible at about the same voltage (about 60 v.) as the anode glow;

(2) the intensity of the cathode glow appears to be about equal to that of the anode glow at the same voltage; and

(3) the distribution of the cathode glow over the surface of the electrode is sometimes different from that of the anode glow.

25-cycle A.C. was used in these experiments, and the mean current through the rectifier was ·3–·5 amp.

11. *Discussion of the Results.*

One of the most interesting features of the glow discharge in the electrolytic rectifier is that it takes place between electrodes which are about 10^{-6} cm. apart (section 4). This results in an abnormally strong electric field—about 10^8v./cm.,—and, consequently, the application of a relatively weak magnetic field produces no observable effect (section 8).

This glow discharge also differs from the ordinary glow discharge in that the oxygen is probably at a pressure of many atmospheres (section 6). The electrostatic attraction between the electrolyte and the electrode might account for this high pressure. Moreover, the mean free path of an electron in oxygen is about ·00005 cm. at atmospheric pressure so that at this pressure about 98 per cent. of the electrons would cross the oxygen layer without colliding with oxygen molecules. This percentage seems much too high, and provides an additional reason for supposing that the pressure of the oxygen is greater than 1 atmos.

It is interesting to note that equation (A) (section 5) is of the same *form* as the well-known parabolic relation between the P.D. and current for an ordinary glow discharge between parallel plate electrodes [5]. The values of the constants for this case do not apply to the rectifier discharge, but this is not surprising as the conditions of the two discharges are so different.

It is difficult to say precisely how the glow is produced. In the oxygen layer the oxygen may be in the atomic or molecular state, and the electrons may be free or associated with oxygen atoms forming negative ions. Negative ions are usually found at high pressures, but in this case they may not be formed owing to the thinness of the layer. The relation between intensity of glow and current ought to give some information about the mechanism of the discharge [6], but the experimental curves are rather inconclusive, although they suggest a linear relation. It is probable that the glow is produced by the ionization of oxygen molecules by collision with electrons, and the subsequent recombination of the electrons with the

ionized molecules; but complete experimental evidence cannot be given for this statement at present.

Some of the facts mentioned in section 11 are of interest in connexion with the electrochemical and electron theories of the rectifying action. To put the matter very briefly, rectification, on the electrochemical theory, is due to oxidation and reduction. The positive half-cycle forms a high-resistance layer of oxide and oxygen, while the negative half-cycle reduces this layer and a large current passes. On the electron theory, rectification occurs because the gas layer is bounded by a metal on one side and by an electrolyte on the other. The metal has a plentiful supply of free electrons, while the electrolyte contains only ions. The positive half-cycle is unable to drive the relatively massive negative ions of the electrolyte through the gas, but the negative half-cycle acts on the mobile electrons of the metal and a large current flows through the gas. Now, the glow is seen during the negative half-cycle, so that the oxygen layer does not disappear as it is supposed to do in the electrochemical theory. The electron theory also does not seem to be entirely satisfactory. If the whole current passes through the oxygen layer, a difference in the intensity of the anode and cathode glows might reasonably be expected, as the current during the negative half-cycle may be hundreds of times as great as that during the positive half-cycle. In order to account for all the facts a new theory of the rectifying action is required, probably involving both the electrochemical and electron hypotheses, but it is not proposed to attempt to formulate such a theory here.

In conclusion, the author wishes to express his gratitude to Professor Taylor Jones for his kind assistance, which has proved invaluable. The work was performed in the Research Laboratories of the Natural Philosophy Department of Glasgow University.

References.

(1) E. H. Robinson, Exp. Wir. pp. 889–892 (Nov. 1925).
(2) E. M. Dunham, Phys. Rev. pp. 819–822 (May 1929).
(3) Jolley, 'Alternating Current Rectification'; Guntherschulze, 'Electric Rectifiers and Valves.'
(4) W. M. Hicks, 'The Analysis of Spectra,' p. 77.
(5) Aston and Watson, Proc. Roy. Soc. A, lxxxvi. p. 168 (1912).
(6) J. Thomson, Phil. Mag. p. 988 (Dec. 1929).

July 1930.

XCIII. *Rates and Temperature Coefficients of the Catalytic Decomposition of Ammonia over Molybdenum, Tungsten, and Promoted Iron.* *By* C. H. Kunsman, E. S. Lamar, *and* W. Edwards Deming *.

THE decomposition of ammonia on hot surfaces can be treated kinetically, since it is a reaction of the simpler form, the reacting substance and the products being gases. The results herein described should be of interest in the study of catalysts for the ammonia reaction. The applicability to surface reactions of concepts commonly accepted in homogeneous reactions is considered.

Perman and Atkinson †, and Bodenstein and Kranendieck ‡, studying the decomposition of ammonia in porcelain and quartz vessels from 677° to 1111° C., concluded that the observed rate could be accounted for by a wall or surface reaction.

We are indebted to Sir William Hardy for establishing the chemistry and physics of a fourth state, surfaces, in comparison with gases, liquids, and solids. The present method of investigating heterogeneous reactions and interpreting their results is an outgrowth of work carried on by Hinshelwood § and his collaborators. Burk ‖ and Schwab ¶ have studied the ammonia reaction with the object of determining the order of the reaction and the effect of the products of reaction. Reports of similar tests have been reported by Kunsman **.

Apparatus.

The essential parts of the apparatus that was used for these catalytic studies are shown in fig. 1. The arrangement consists essentially of a decomposition chamber of about 1 litre capacity, containing and supporting the surfaces upon which the kinetics of the decomposition of ammonia

* Communicated by the Authors.

† Perman and Atkinson, Proc. Roy. Soc. lxxiv. p. 110 (1904).

‡ Bodenstein and Kranendieck, 'Nerst Festschrift,' Wilhelm Knapp (1912).

§ Hinshelwood, "Kinetics of Chemical Changes in Gaseous Systems," Oxford University Press (1926), hereafter referred to as Hinshelwood, 'Kinetics.'

‖ Burk, Proc. Nat. Acad. Sci. xiii. p. 67 (1927).

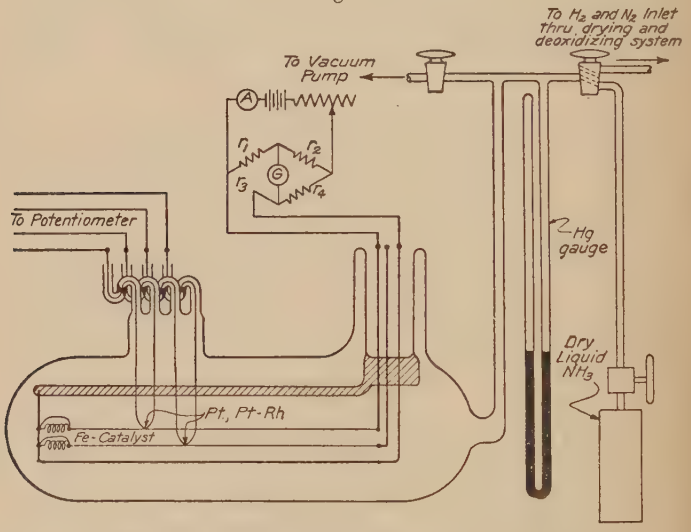
¶ Schwab, *Zs. Physik. Chem.* cxxviii. p. 161 (1927).

** Kunsman, J. Am. Chem. Soc. l. p. 2100 (1928); li. p. 688 (1929); J. Frank, Inst. cciii. p. 635 (1927); J. Chem. Education, vi. p. 623 (1929).

were investigated. Three chambers were actually employed, identical in construction except that one contained drawn filaments of molybdenum, one contained a tungsten filament, and the other, as illustrated, contained platinum strips coated with iron catalysts. The molybdenum wires were 0·0308 cm. in diameter, and were furnished by the Fansteel Products Company. The tungsten filament was 0·254 mm. in diameter, and was furnished by the General Electric Company. The cross-section of the platinum strips was 0·46 × 0·10 mm.

The apparatus was constructed of pyrex with heavy tungsten wires leading into the decomposition chamber. The tungsten leads formed a part of the support of the

Fig. 1.



Apparatus for the study of the decomposition of ammonia on hot surfaces.

surfaces, and enabled the catalyst surface to be heated to a desired temperature from a storage battery. The filaments or coated strips were kept taut by means of molybdenum springs. The shunted platinum strip carried most of the current, so that no part of the apparatus was sufficiently hot to decompose ammonia except the filaments or coated strips.

As the rate of a chemical reaction and the corresponding kinetics are so vitally dependent on the temperature, every precaution was taken to determine the temperature of the hot surface and keep it constant throughout a test.

Three methods were used to determine the temperature: (1) direct observation with a Leeds and Northrup optical pyrometer, calibrated at the Bureau of Standards, and corrected for the emissivity of the surface and absorption by the glass; (2) employing the temperature coefficient of the resistance of tungsten or molybdenum; and (3) using a thermocouple welded to the filament or coated strip. In the last method 0·005 cm. diameter Pt, Pt–Rh wire was used, the juncture being located at the hot surface in the middle of its length. As some difficulty is experienced in making the thermocouple lead seals through pyrex, the form of the seal was modified as shown in fig. 1 to form a small cup about each wire. This cup may be filled with mercury or deKhotinshy wax, either of which will stop any leak that may result from an imperfect metal to pyrex seal.

Since the hydrogen formed as a decomposition product is a better conductor of heat than ammonia or nitrogen, it is necessary to increase the current through the filament or coated strip as the decomposition progresses, in order to keep the resistance and temperature of the filament constant. The Wheatstone bridge arrangement shown in fig. 1 enables this to be done quickly and easily. The coated strip is made one resistance r_3 of the bridge, comparable with r_4, but small in comparison with r_1 and with r_2.

A minimum number of stopcocks was used. A mercury trap, which is not shown in fig. 1, separated the decomposition chamber and manometer from the rest of the apparatus during a decomposition run. The decomposition chamber and connecting parts were first thoroughly heated in an oven and evacuated to a low pressure. Very pure dry ammonia was then admitted to a pressure of about one-third of an atmosphere, and the rate of decomposition was measured for a given temperature by the increase of pressure noted on the manometer at various moments as the reaction progressed. Thus the pressure in the tube is obtained as a function of the time.

The coated strips were much more active catalysts than the drawn filaments, and it may be well to describe in detail their preparation. Incidentally these catalysts are among the better ones developed for the commercial synthesis of ammonia. They are made from fused pure artificial magnetite, to which about 1 per cent. of aluminium oxide and 1 per cent. of an alkali oxide, usually of potassium, has been added in the fusion process. Very uniform coated surfaces can be obtained from the oxide mixture when ground to 300 mesh or finer, reduced by hydrogen, and

mixed with paraffin. This is applied to the electrically heated twisted platinum strip with a glass rod. The strip should be only hot enough to vaporize the paraffin. After obtaining a uniform layer over the entire length of the strip it should be raised to a dull red temperature in air. A bright hot spot will develop, due to the rapid oxidation of the finely divided iron particles, and will spread over the entire surface. A temperature sufficiently high to sinter or fuse the coating to the strip is thus reached. This procedure may be repeated until the desired thickness has been obtained. Such a coating, after being reduced in hydrogen, is very stable, and is uniform in thickness throughout its length, but it does not furnish as active a catalytic surface as one obtained by coating with the unreduced mixture, for in the latter case the particles are not as firmly attached. The procedure for coating the strips with the unreduced oxides is similar to that just described, but the coating is not subjected to the sintering process. In either case the coating of oxides must be reduced in order that it may serve as a catalyst. The reduction should be carried on at a dull red temperature for about twelve hours in hydrogen. The coated platinum strips used in these experiments were in every case covered originally with the unreduced mixture. There was about 1 gram of oxides on each strip.

By means of the very active coated strips, on the one hand, and the relatively inactive molybdenum and tungsten filaments on the other, decomposition runs were made from 475° to 1295° C.

Theory of Surface Kinetics.

In this discussion let E denote $-\mathrm{R}d\ln k : d\mathrm{T}^{-1}$, where k is the reaction velocity at temperature T. Arrhenius found the plot of $\ln k$ vs. T^{-1} to be a straight line with many homogeneous reactions, and he called E the "heat of activation." With a heterogeneous reaction the plot often has some curvature, and Hinshelwood * calls E at any point the "apparent heat of activation" for that temperature. One cause of this curvature, mentioned by Hinshelwood †, may be that the observed reaction is a composite one made up of two or more concurrent reactions differently influenced by temperature. Another cause may be that the fractions of the active surface that are covered by the reactants and

* Hinshelwood, 'Kinetics,' p. 176.
† Hinshelwood, 'Kinetics,' p. 46.

products may vary with temperature. In this paper the second cause is treated.

The "true heat of activation" is the value of E that would be observed in a simple reaction where the fraction of the active surface covered by each product and reactant, and consequently where the inhibition by the products, is independent of the temperature.

Hinshelwood * discusses two special cases of inhibition by the adsorbed products. By treating it in a more general way we arrive at the second explanation of curvature, and also are enabled to compute the true heat of activation when the reaction is a simple one (not composite).

In this paper we shall give this more general treatment, and then use the results to find the true heat of activation for the decomposition of ammonia on different catalysts, and to estimate the difference in the heats of adsorption for ammonia and hydrogen.

We shall use the following symbols, with the subscripts 0 for the reactant, and 1, 2, . . ., n for the n products of the decomposition :—

a_i = rate of condensation of gas i onto unit uncovered area of the catalytic surface. a_i may vary with pressure, but scarcely with temperature †.

σ_i = fraction of the active surface covered by gas i, averaged with respect to time.

$b_i e^{-\lambda_i/RT}$ = rate of evaporation of gas i from unit area completely covered at temperature T.

λ_i = heat of desorption for gas i, here treated as being constant.

$$B_i = b_i a_i^{-1} e^{-\lambda_i/RT}, \qquad dB_i/dT^{-1} = -\lambda_i B_i/R.$$

We shall assume that the establishment of adsorption equilibrium is rapid compared with the rate of removal or deposition of molecules by chemical change, and we shall neglect the back reaction.

At adsorption equilibrium, while the partial pressures are constant,

$$\left(1 - \sum_0^n \sigma_i\right) a_i = \sigma_i b_i e^{-\lambda_i/RT}, \qquad i = 0, 1, 2, \ldots, n ; \qquad (1)$$

* Hinshelwood, 'Kinetics,' pp. 176–178.
† Hinshelwood, 'Kinetics,' p. 144.

i. e.,

$$\left.\begin{aligned}
&\sigma_0(1+B_0)+\sigma_1+\sigma_2+\ldots+\sigma_n=1,\\
&\sigma_0+\sigma_1(1+B_1)+\sigma_2+\ldots+\sigma_n=1,\\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\\
&\sigma_0+\sigma_1+\sigma_2+\ldots+\sigma_n(1+B_n)=1.
\end{aligned}\right\}\quad\ldots\quad(2)$$

Solving these for σ_0, σ_1, σ_2, ...,

$$\sigma_i=B_0/AB_i,\qquad i=0,\ 1,\ 2,\ \ldots,\ n,\quad\ldots\quad(3)$$

where

$$A=1+B_0+B_0/B_1+\ldots+B_0/B_n.\quad\ldots\quad(4)$$

If k denotes the observed forward reaction velocity, Q the true heat of activation, and if the mechanism of reaction remains the same,

$$k\propto\sigma_0 e^{-Q/RT},\quad\ldots\quad(5)$$

$$\frac{d}{dT^{-1}}\ln k\equiv-E/R=-Q/R+\frac{d}{dT^{-1}}\ln\sigma_0.\quad\ldots\quad(6)$$

$$\begin{aligned}
E&=Q-R\frac{d}{dT^{-1}}\ln\sigma_0=Q+R\frac{d}{dT^{-1}}\ln A\\
&=Q+RA^{-1}.dA/dT^{-1}\\
&=Q-A^{-1}\left\{\lambda_0B_0+\sum_1^n(\lambda_0B_0-\lambda_iB_0)B_i^{-1}\right\}\\
&=Q-A^{-1}\left\{\lambda_0(A-1)-B_0\sum_1^n\lambda_iB_i^{-1}\right\}\\
&=Q-\lambda_0(1-\sigma_0)+\lambda_1\sigma_1+\lambda_2\sigma_2+\ldots+\lambda_n\sigma_n\\
&=Q-\lambda_0+\sum_0^n\lambda_i\sigma.\quad\ldots\quad(7)
\end{aligned}$$

If σ_0, σ_1, ..., σ_n all change as T changes, then E, and hence the slope $d\ln k:dT^{-1}$, will vary with T, and the $\ln k$ vs. T^{-1} plot will be curved, even though the reaction be a simple one. In case the λ_i are all about equal, and $\Sigma\sigma_i$ remains constant, E will be constant, and the plot will be a straight line. If the λ_i are all equal and $\Sigma\sigma_i=1$, $E=Q$.

This formula contains the two special cases discussed by Hinshelwood.

For discussion of the decomposition of ammonia let subscripts 0, 1, 2 refer to ammonia, hydrogen, nitrogen.

If σ_2 is practically zero, and if $\sigma_0+\sigma_1$ remains practically unity, then $\sigma_0/\sigma_1=B_1/B_0$ (from eq. 3) becomes

$$\sigma_0/(1-\sigma_0)=B_1/B_0;$$

whence

$$\frac{a_0}{a_1}=\frac{\sigma_0}{1-\sigma_0}\cdot\frac{b_0}{b_1}e^{(\lambda_1-\lambda_0)/RT}\equiv\frac{\sigma_0}{1-\sigma_0}g(T). \quad . \quad . \quad (8)$$

By making use of Langmuir's conclusion that practically every molecule that strikes a surface condenses, a_i is the number of molecules of gas i that strike unit area of the catalyst surface per second. Consequently, from kinetic theory and from eq. (8),

$$\frac{a_0}{a_1}=\frac{p_0}{p_1}\left(\frac{M_1}{M_0}\right)^{\frac{1}{2}}=\frac{\sigma_0}{1-\sigma_0}g(T); \quad . \quad . \quad . \quad (9)$$

whence

$$\sigma_0=\left[\frac{p_1}{p_0}\left(\frac{M_0}{M_1}\right)^{\frac{1}{2}}\cdot g(T)+1\right]^{-1}. \quad . \quad . \quad . \quad (10)$$

At constant temperature, $k\propto\sigma_0$ (eq. 5), so we may write

$$k\equiv c(T)\left[\frac{p_1}{p_0}\left(\frac{M_0}{M_1}\right)^{\frac{1}{2}}g(T)+1\right]^{-1},$$

or

$$1/k=\frac{g(T)}{c(T)}\cdot\left(\frac{M_0}{M_1}\right)^{\frac{1}{2}}\frac{p_1}{p_0}+1/c(T). \quad . \quad . \quad . \quad (11)$$

So if $1/k$ is plotted against $\frac{p_1}{p_0}\left(\frac{M_0}{M_1}\right)^{\frac{1}{2}}$ as abscissas, there should result a straight line whose intercept on the $1/k$ axis is $1/c(T)$, and whose slope is $g(T)/c(T)$. Thus one can find $g(T)$ and $c(T)$. σ_0 as a function of T can then be found from eq. (10).

$c(T)=k/\sigma_0$ is the rate of decomposition on unit area covered with ammonia. $-R\,d\ln c(T):d(T^{-1})$ should be the true heat of activation Q. If $\sigma_2=0$ and $\sigma_0+\sigma_1=1$ in (7),

$$E=Q+(\lambda_1-\lambda_0)(1-\sigma_0). \quad . \quad . \quad . \quad (12)$$

Knowing E and σ_0 at particular values of T and of p_1/p_0, and knowing Q, we can easily find $\lambda_1-\lambda_0$ from eq. (12). But this is not a very accurate method, because $\lambda_1-\lambda$ is thus made the small difference between two relatively large quantities.

Another method of getting $\lambda_1-\lambda_0$ comes from the definition of $g(T)$ in eq. (8). If $\ln g(T)$ vs. T^{-1} be plotted, $R\,d\ln g(T):d(T^{-1})=\lambda_1-\lambda_0$.

End Correction for the Heated Filament.

The correction for cooling at the ends of an 18 cm. molybdenum filament while being used as a catalyst has been investigated *. The equivalent length effective at the maximum temperature $T_{max.}$, which is the temperature in the middle, was computed by averaging the rate of reaction along the full length ; thus, if k is the reaction rate over an element Δx at a distance x from one end, and $\bar{k}$ the reaction rate at $T_{max.}$, the equivalent length is $\Sigma k\Delta x/\bar{k}$. The results follow closely the law $y=ax^n$, with $a=\cdot099448$ and $n=1\cdot5464$, x being $(10^4/T_{max.})$ and y being the end correction (for both ends) in cm., $y=18$ cm. minus equivalent length. One can expect the end correction to be independent of the length of the filament provided it is not too short. A different filament would have new constants on account of having different heat conductivity, resistivity, and catalytic action, but the equation for molybdenum could probably be used for tungsten with some confidence, because the characteristics of molybdenum and tungsten are not too far different.

A portion of the increase in reaction rate observed with increase in temperature is due to the decrease in end correction. It was thought best to present the experimental results and deductions for molybdenum and tungsten as if there were no end correction, and then to introduce the refinement. It was not necessary to correct the figures for the promoted iron catalysts, because the platinum strips were coated so that the whole coated length when heated appeared to be of uniform redness.

The end correction for this work is very easily applied. If $c'(T)$ and Q' are the uncorrected values of $c(T)$ and Q, and if L is the total measured length of filament, then

$$c(T)=c'(T)L/(L-y)=c'(T)\,L/(L-ax^n),$$

$$\frac{d}{dx}\ln c(T)=\frac{d}{dx}\ln c'(T)+nax^{n-1}L^{-1};$$

so

$$Q=Q'-10^4R\,nax^{n-1}L^{-1}. \quad . \quad . \quad . \quad . \quad (13)$$

Here $n-1=\cdot5464$ and the range of x is never great, so the end correction term is considered to be independent of x, which would make Q and Q' differ by a constant; in other words, if the plot of $\ln c(T)$ vs. T^{-1} is a straight line, the plot of $\ln c'(T)$ vs. T^{-1} would also be straight. In practice

* E. S. Lamar and W. E. Deming, "Temperature Distribution along a Heated Filament used as a Catalyst," Phil. Mag. p. 28 (Jan. 1930).

the average value of x for a set of decomposition runs was used in the correction term.

The quantity $\varphi(T)$ as defined in eq. (8) is dimensionless, and is not affected by the end correction.

Evaluation of Q *and of* $\lambda_0 - \lambda_1$ *on Molybdenum.*

Two sets of data were taken using two different molybdenum filaments. One (*a*), 18 cm. long, had been used as a catalyst several months, and the other (*b*), 12 cm. long, was new.

In a previous article * it was shown by one of the authors that an initial excess of nitrogen has little or no effect on the time for half decomposition. His experiments have been repeated, and this conclusion corroborated; so it appears that nitrogen is adsorbed only slightly in the presence of hydrogen and ammonia. Therefore we feel justified in putting $\sigma_2 = 0$. But an initial excess of hydrogen lengthens the time for half decomposition, so $\sigma_1 \neq 0$.

We found that if the temperature of the filament is kept constant, then over quite a wide range of initial pressures of ammonia (from 12 to 30 cm.) the time for half decomposition is proportional to the initial pressure of ammonia. This means that the average rate of decomposition over the half-time is independent of the initial pressure of ammonia. Since $k \propto \sigma_0$, and since k does not increase with initial ammonia pressure, the maximum available surface must remain covered with hydrogen and ammonia, *i. e.*, $\sigma_0 + \sigma_1 = 1$ and $\sigma_2 = 0$. Still another proof of this point was obtained by testing the data by means of eq. (10), from which it can be seen that if the original assumptions are correct, at a particular temperature k should be a function of p_1/p_0 only, regardless of the initial ammonia pressure. This was found to hold over the pressure range mentioned above.

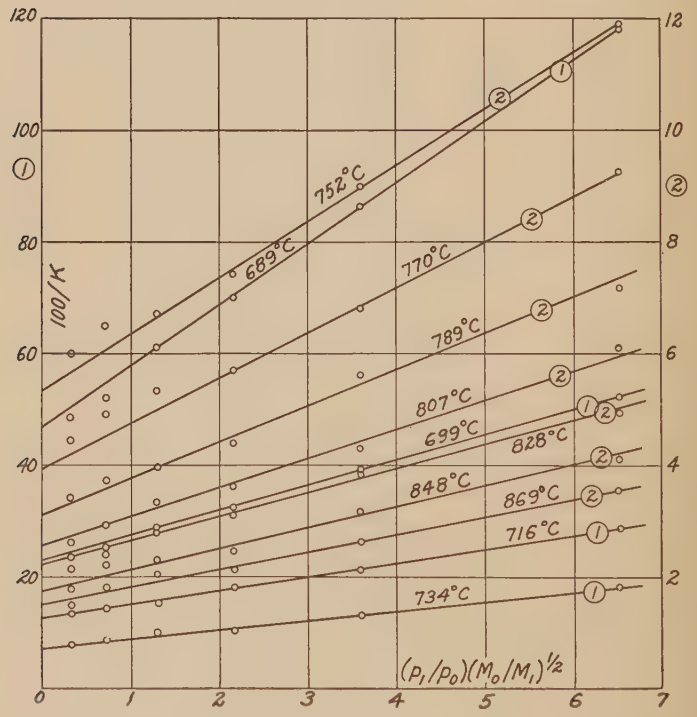
k, which represents the speed of decomposition at any instant, is proportional to $dp : dt$, the time rate of increase of pressure in the tube. We put $k = dp : dt$, the slope of a pressure vs. time plot of the original data. In our work k and $dp : dt$ refer to unit area of catalyst surface as determined by the geometrical dimensions of the filament.

Figs. 2 and 3 show the $1/k$ vs. $(p_1/p_0)(M_0/M_1)^{\frac{1}{2}}$ isotherms. Each point is the average of two runs, taken one after another, beginning with the highest temperature and

* Kunsman, J. Amer. Chem. Soc. l. p. 2100 (1928); li. p. 688 (1929); J. Frank, Inst. cciii. p. 365 (1927); J. Chem. Education, vi. p. 623 (1929).

working down to the lowest, then working back up again to the highest. Nine different temperatures, ranging from 681° to 926° C., were used for filament *b*, and twelve, ranging from 689° to 891° C., for filament *a*. Over the time interval used for the entire set of observations the activities of neither catalyst decreased a measurable amount. The curve for 891° C. is omitted from fig. 2 because it happens almost to coincide with another one plotted to a different scale.

Fig. 2.



k^{-1} vs. $(p_1/p_0)\,(M_0/M_1)^{\frac{1}{2}}$ for used molybdenum filament (*a*).

k=reaction rate in cm. Hg per minute per square centimetre of catalyst surface.

p_0, p_1=partial pressure of ammonia, hydrogen.

M_0, M_1=molecular weight of ammonia, hydrogen.

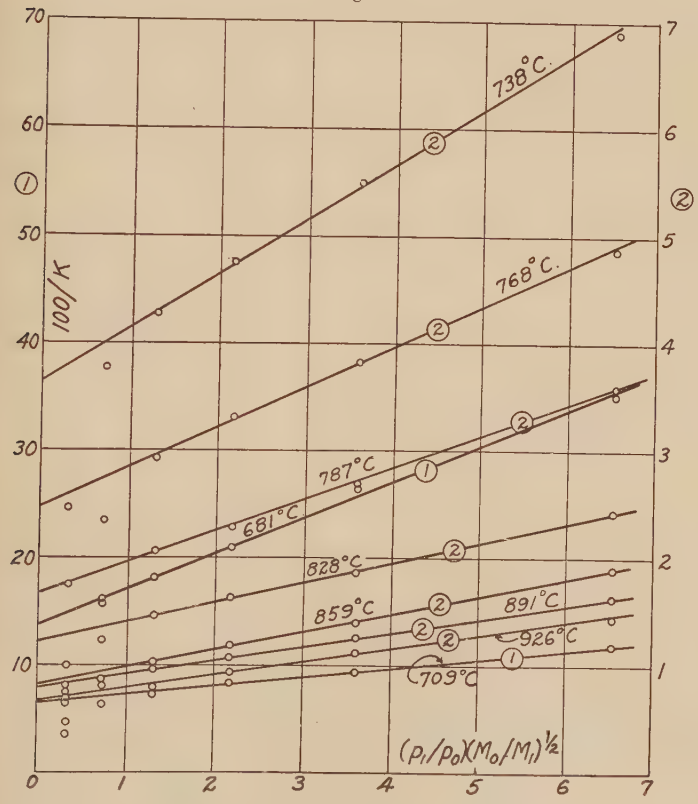
The numbers in the circles designate the scale for the ordinates.

The temperature of the filament, as measured by it resistance, was held constant to within three degrees during a run. The initial ammonia pressure was 26·6 cm. Hg for all runs.

From the isotherms of figs. 2 and 3 we find $g(T)$ and $c'(T)$ by the method previously explained.

Near the beginning of a run, where $(p_1/p_0)\,(M_0/M_1)^{\frac{1}{2}}$ is small, there is superimposed upon the rate of reaction an apparent rate (an increase in pressure) due to the heating of the gas in the tube immediately after the filament is

Fig. 3.



k^{-1} vs. $(p_1/p_0)\,(M_0/M_1)^{\frac{1}{2}}$ for new molybdenum filament (*b*).

k = reaction rate in cm. Hg per minute per square centimetre of catalyst surface.

p_0, p_1 = partial pressure of ammonia, hydrogen.

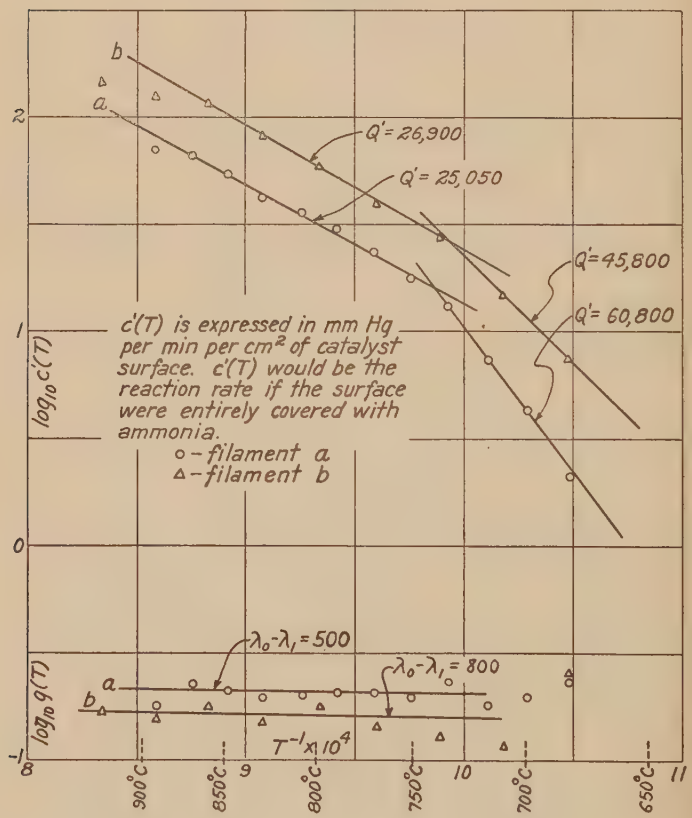
M_0, M_1 = molecular weight of ammonia, hydrogen.

The numbers in the circles designate the scale for the ordinates.

turned on. At the lower temperatures this source of error is noticeable only at the beginning of a run. At the highest temperatures half decomposition is completed before the gas

in the tube has reached temperature equilibrium. Since it takes time for the products of the reaction to diffuse away from the filament, the value of p_1/p_0 near the filament is not the value of p_1/p_0 in the tube. This difference is negligible except at the highest temperatures, when the reaction is very fast. In getting $c'(T)$ and $g(T)$ from figs. 2 and 3 the

Fig. 4.



Evaluation of Q^1 and of $\lambda_0 - \lambda_1$ for molybdenum.

right-hand portions only of the curves were considered, because the errors are least effective there.

$c(T)$ is the value that k would have at temperature T if the filament were entirely covered with ammonia. The $\ln c'(T)$ vs. T^{-1} and the $\ln g(T)$ vs. T^{-1} curves are shown in fig. 4. The $c'(T)$ points for each filament determine two

straight lines, which break at about 1013° K. (740° C.) for *a* and at about 1008° K (735° C.) for *b*. The portions on the low temperature sides of the breaks seem to indicate the existence of molybdenum nitride, probably formed from the ammonia. We conclude that at temperatures above the breaks the nitride ceases to exist in the presence of hydrogen. The deviations of the extreme high-temperature points from the straight line are due to the second source of error mentioned in the preceding paragraph, since at these temperatures the reaction is very fast and the products do not have a chance to diffuse from the filament as fast as they are formed. There are no perceptible breaks in the $g(T)$ curves.

The following tabulation is derived from fig. 4:—

L.	Mo. Fil. *a*. 18 cm.	Mo. Fil. *b*. 12 cm.
Q uncorrected:		
High temperature.....	25,050	26,900
Low temperature	60,800	45,800
Average $10^4/T$:		
High temperature.....	9·2	9·2
Low temperature	10·4	10·4
Q corrected (eq. 13):		
High temperature	24,500	26,050
Low temperature	60,200	44,900
$\lambda_0-\lambda_1$	500	800

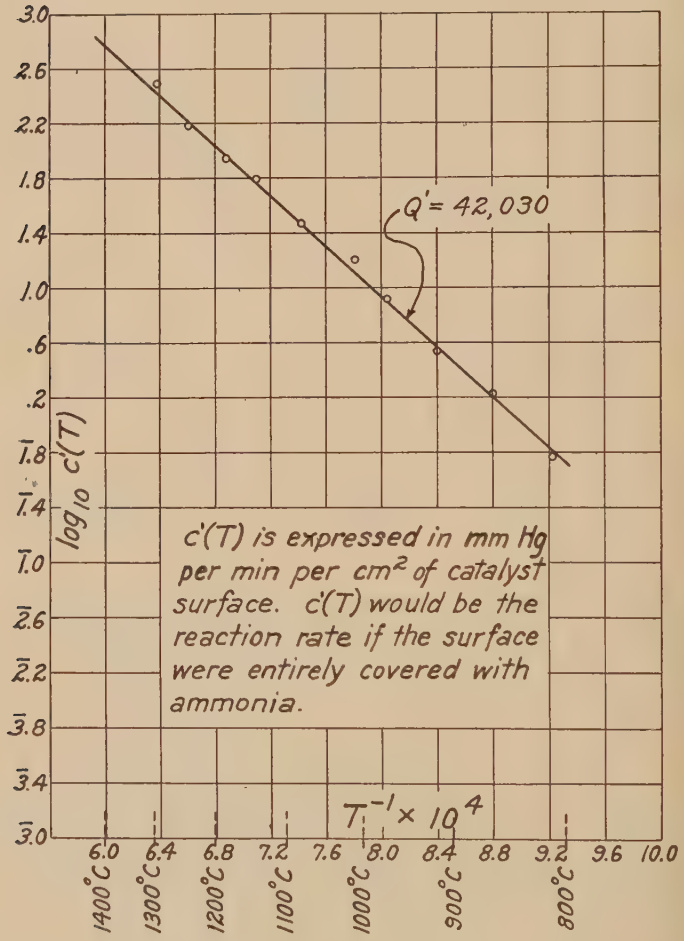
Filament *b*, the new one, was more active than *a*, and had a higher heat of activation. The metal composing a filament tends to form larger and larger crystals as it is used, and this lowers its activity, probably because its available surface area is thus decreased.

Evaluation of Q *for a Tungsten Filament.*

The best available data for tungsten were treated in the same manner as the data on molybdenum. The same arguments that were used to show that nitrogen is only slightly adsorbed, if at all, and that the active surface remains entirely covered by hydrogen and ammonia for the molybdenum filament, hold good for tungsten. The ten decomposition runs were made, beginning with the highest temperature (1295° C.) and working down to the lowest (810° C.). A check-back on the highest temperature showed that there had been no measurable change in activity. The $1/k$ vs. $(p_1/p_0)\,(M_0/M_1)^{\frac{1}{2}}$ plot is omitted because it is a series of straight lines similar to those for molybdenum. The

log $c'(T)$ vs. T^{-1} curve is fig. 5, whose slope gives Q (uncorrected) $=42{,}030$ calories per mol. The length of the tungsten filament was 18 cm., and the average of $10^4/T$ is easily estimated from the figure to be about 7·8, whence

Fig. 5.



Evaluation of Q^1 for tungsten.

by eq. (13) Q (corrected) $=41{,}500$. An attempt was made to evaluate $\lambda_0 - \lambda_1$, but the curvature of the p vs. t curves was so small that $g(T)$ could not be determined accurately. Furthermore, there was only one run at each temperature,

and this fact lessened the precision. As far as we could tell, $\lambda_0-\lambda_1$ is small, probably not greater than 1500.

Evaluation of Q *and of* $\lambda_0-\lambda_1$ *for Iron Catalyst no.* 1.

The promoted iron catalyst mixture no. 1 in the unreduced form consisted of a mixture of the oxides of iron, aluminium, and potassium, in the ratio 98·69 : 1·05 : 0·26 by weight. The coated strip, 19 cm. in length, was reduced in hydrogen at dull red heat. The activity of such a catalyst is highest immediately following reduction, after which it decreases, rapidly at first, and then more and more slowly. With our catalyst a temperature calibration was taken immediately after reduction, so by the time the decomposition runs were made it was in fairly stable condition, but its activity was somewhat lower than it was initially.

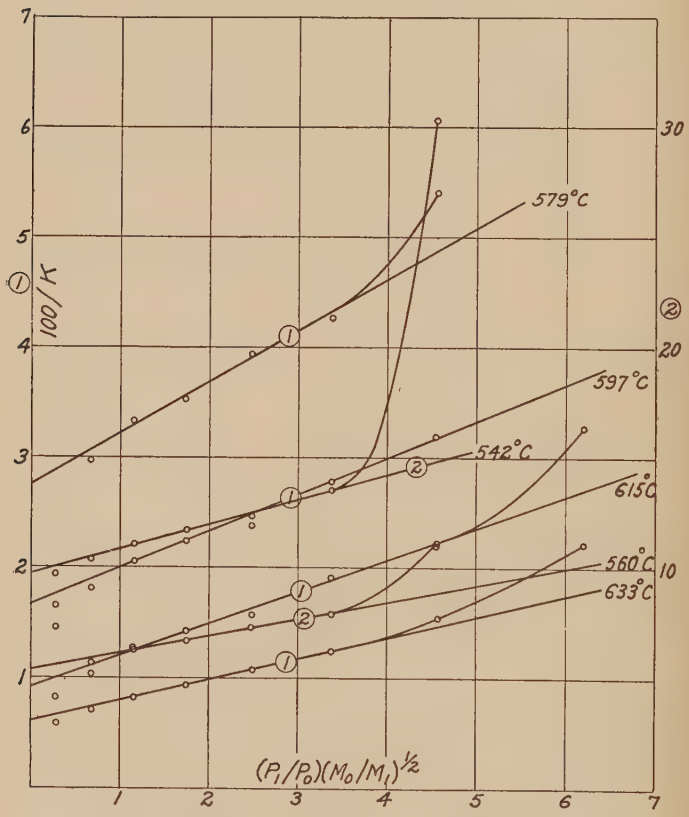
The processes that take place on an iron mixture may be more complicated than those encountered on the surface of a drawn metal wire, such as the molybdenum and tungsten filaments already discussed. On the latter the surface conditions remain very uniform, but on the former the thermal conduction from the surface increases with the progress of the reaction, and the temperature of the entire surface decreases slightly while the resistance and temperature of the platinum strip remain constant. The upward curvature in figs. 6 and 9 is thus attributed to a physical change in surface conditions rather than to a change in $\sigma_0+\sigma_1$. It is to be remembered that $g(\mathrm{T})$ is dimensionless, and is thus independent of the amount of surface covered, so values of $g(\mathrm{T})$ obtained from slopes and intercepts of tangents taken at different points along a single $1/k$ v/s$_0$. $p_1/p_0(\mathrm{MM}_1)^{\frac{1}{2}}$ would be the same if the curvature were due to a change in $\sigma_0+\sigma_1$. But the values of $g(\mathrm{T})$ obtained from figs. 6 and 9 do depend on the point of tangency, so it seems certain that the departure of these curves from linearity is due to a change in surface conditions, and not to a change in $\sigma_0+\sigma_1$.

The curves in fig. 6 have well-defined straight portions, which indicate constant surface conditions over part of each run. The $c(\mathrm{T})$ and $g(\mathrm{T})$ determined from these straight portions refer to the surface in its constant state.

The runs on catalyst no. 1 were taken at six different filament temperatures, one after another, over 91° range, beginning with the highest temperature and working down to the lowest, then working back to the highest. Thus two runs were taken at each temperature. Over the interval of time required for these runs the activity at the highest

temperature decreased about 1·5 per cent., which is barely outside the experimental error. The effect of this gradual shift in activity was eliminated by taking the average of the two runs at each temperature. As before, the temperature of the filament was held constant to within several degrees during a run. The initial ammonia pressure was 26·6 cm.

Fig. 6.

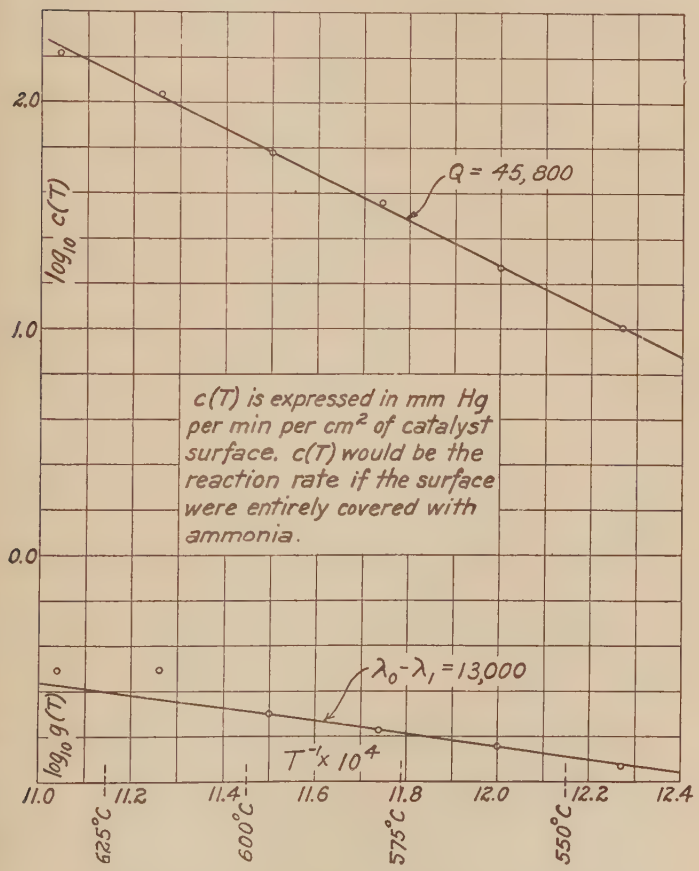


k^{-1} vs. $(p_1/p_0)(M_0/M_1)^{\frac{1}{2}}$ for promoted iron catalyst no. 1.
k = reaction rate in cm. Hg per minute per square centimetre of catalyst surface.
p_0, p_1 = partial pressure of ammonia, hydrogen.
M_0, M_1 = molecular weight of ammonia, hydrogen.
The numbers in the circles designate the scale for the ordinates.

Hg for all runs. All the data were taken in exactly the same manner.

The results are shown graphically in fig. 6. The straight portions of these curves determine $c(T)$ and $g(T)$, whose logarithms are plotted as functions of T^{-1} in fig. 7. The slopes of the straight lines determined by these points give

Fig. 7.



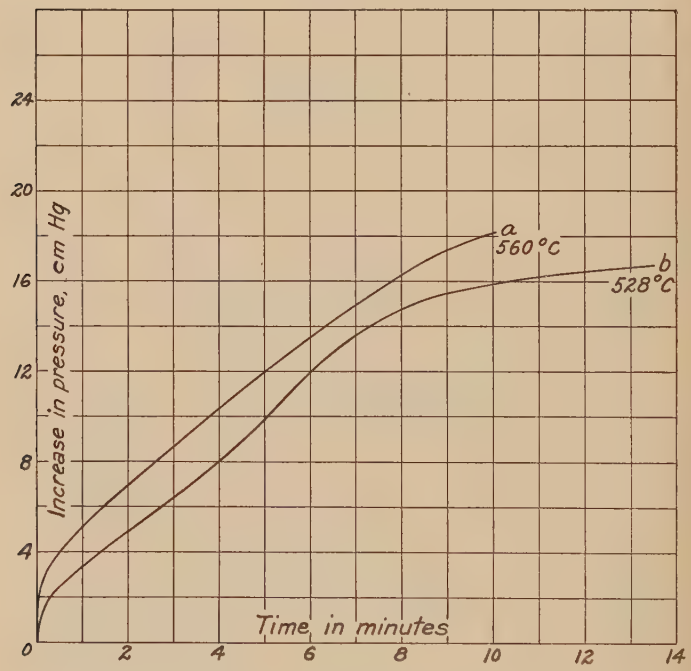
Evaluation of Q and of $\lambda_0 - \lambda_1$ for promoted iron catalyst no. 1.

$Q = 45{,}800$ calories per mol., and $\lambda_0 - \lambda_1 = 13{,}000$. As mentioned before, it is not necessary to make an end correction for Q for the iron catalysts.

Since the temperatures were comparatively low, it was suspected that the decomposition may have taken place on a nitride rather than on an iron surface. An attempt was

made to test for such a nitride at each of the temperatures used in the decomposition runs. The procedure at a particular temperature was as follows:—A decomposition run was allowed to go halfway to completion, then the filament was turned off and the products were pumped out. Hydrogen was then admitted, and the filament heated to 633° C., the highest temperature used. It was expected that the hydrogen would reduce the nitride to form ammonia, and that the

Fig. 8.



Pressure vs. time curves.

(*a*) Typical for promoted iron after some use.

(*b*) Typical for promoted iron immediately after reduction, its most active condition.

The ordinates are the increase in pressure in the tube above the initial 26·6 cm. Hg.

ammonia would decompose catalytically. There should result, then, an increase in pressure equal to the partial pressure of the nitrogen liberated. Such an increase was observed and measured with a manometer. The above procedure was repeated, stopping the decomposition runs at smaller degrees of completion, and as near as could be

determined the partial pressure of nitrogen was the same in each case. This means that the nitride is probably formed near the beginning of the decomposition run, and that during the remainder the entire active surface is covered with nitride. This conclusion is further substantiated by the fact that within the limits of experimental error the nitride content was the same at each of the different temperatures investigated. The results given in fig. 7, therefore, are probably those for an iron nitride surface as a catalyst.

Fig. 8 shows two pressure vs. time curves: (*a*) is a typical one for the promoted iron just discussed; (*b*) is one for a promoted iron catalyst in its most active condition, immediately after reduction. An interesting phenomenon is apparent in curve (*b*). The first rapid rise in pressure is the temperature effect previously mentioned, but after that it will be observed that there is actually an increase in decomposition rate as the run progresses, which finally levels off fairly sharply. Near the beginning of the run the surface may become covered with a nitride of iron, and, further, the activity of the nitride as a catalyst may be less than the activity of the iron itself. As the run progresses more hydrogen is liberated, which begins to reduce the nitride. As the nitride is reduced, more and more of the iron surface becomes available, and the rate increases until a point is reached at which the hydrogen as a thermal conductor becomes effective in reducing the temperature of the surface. At this point the p vs. t curve begins to level off.

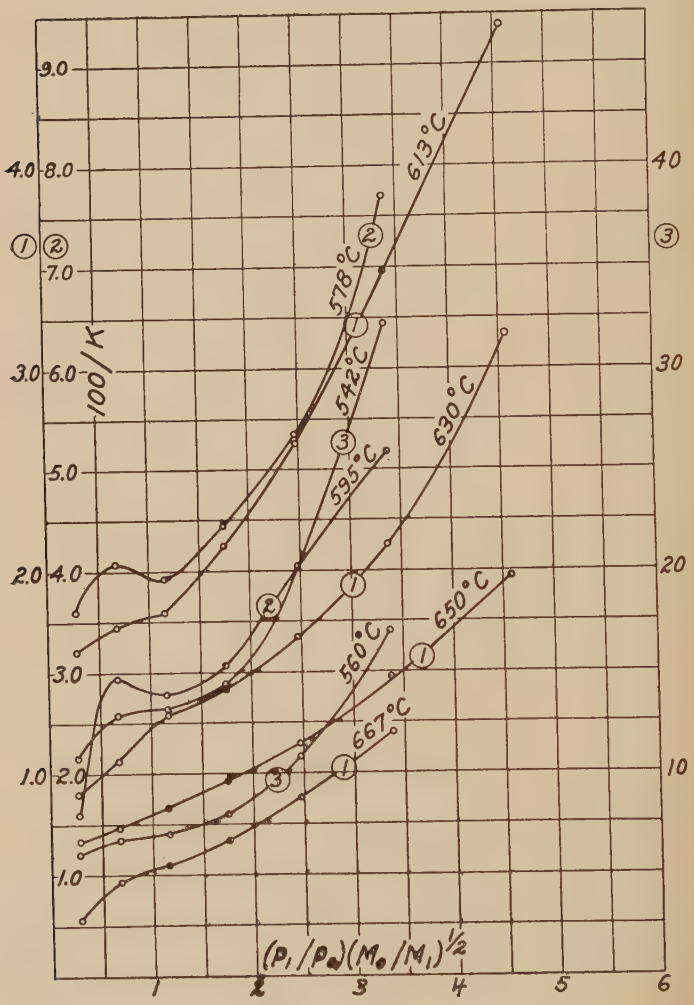
If the above analysis is the correct one, the iron nitride is more readily removed by hydrogen from the more active form of the catalyst than from the less active form.

Evaluation of Q *and of* $\lambda_0-\lambda_1$ *for Iron Catalyst no.* 2.

Application of the theory that was developed in the first part of this paper was made by placing $\sigma_0+\sigma_1=1$ and $\sigma_2=0$—that is, by assuming that the entire active surface remains covered with ammonia and hydrogen. When the $1/k$ vs. $(p_1/p_0)\,(M_0/M_1)^{\frac{1}{2}}$ curves are straight lines the condition of the surface remains invariable. When one of these curves yields varying values of $g(T)$ the surface conditions vary during a decomposition run, and values of Q and of $\lambda_0-\lambda_1$ for the *average* surface are desired. When these curves are replaced by straight lines that best approximate the points along the curves, the slopes and intercepts of these straight lines determine the Q and $\lambda_0-\lambda_1$ that refer to the average surface conditions.

The iron catalyst mixture no. 2 in the unreduced form consisted of the oxides of iron, aluminium, potassium, and molybdenum in the ratio 94·11 : 2·00 : 0·25 : 3·64 by weight.

Fig. 9.



k^{-1} vs. $(p_1/p_0)(M_0/M_1)^{\frac{1}{2}}$ for promoted iron catalyst no. 2.

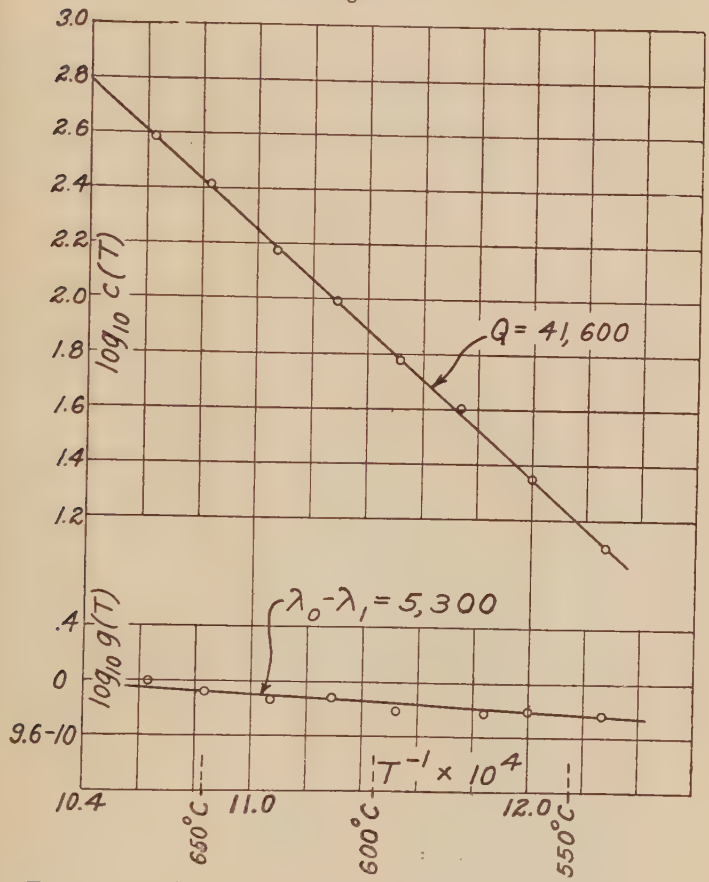
k=reaction rate in cm. Hg per minute per square centimetre of catalyst surface.

p_0, p_1=partial pressure of ammonia, hydrogen.

M_0, M_1=molecular weight of ammonia, hydrogen.

Runs were taken at eight different filament temperatures, one after another over 125° range, beginning with the highest temperature (667° C.) and working down to the lowest (542° C.), then working back to the highest. Thus, two runs were taken at each temperature. Over this interval the activity at the highest temperature decreased 1·5 per

Fig. 10.



Evaluation of Q and of $\lambda_0 - \lambda_1$ for promoted iron catalyst no. 2.

cent., which is barely outside the experimental error. The length of the platinum strip was again 19 cm., and the runs were made in the same manner as those for no. 1.

The $1/k$ vs. $(p_1/p_0)(M_0/M_1)^{\frac{1}{2}}$ curves are shown in fig. 9. The straight lines that replace these curves are not shown,

because they confuse the figure. The slopes and intercepts of these lines determine $c(T)$ and $g(T)$, shown in fig. 10. Q turns out to be 41,600 and $\lambda_0-\lambda_1$ to be 5300.

The authors wish to acknowledge the continual support of Dr. F. G. Cottrell, the director of this laboratory, and the cooperation of other members of the staff in the course of this work.

Summary.

The writers have taken into consideration the condensation on to the catalyst surface and the evaporation therefrom of the products of a catalytic decomposition, and have derived a formula (neglecting the back reaction) for the so-called "true heat of activation," Q, in terms of the temperature coefficient E, and the heats of desorption of the reactant and products. The formula is

$$E = Q - \lambda_0 + \sum_0^n \lambda_i \sigma_i,$$

in which $\lambda_0, \lambda_1, \ldots, \lambda_n$ are the heats of desorption for the reactant and n products, and $\sigma_0, \sigma_1, \ldots, \sigma_n$ are the fractions of the surface covered by the reactant and n products.

They have decomposed ammonia on molybdenum and on tungsten in the form of filaments electrically heated, and on promoted iron catalysts applied on electrically heated platinum strips, and have shown that the adsorption of nitrogen from the gas phase is negligible, but that the active surface remains entirely covered with hydrogen and ammonia during a run within the temperature ranges studied. From theoretical considerations they are able to compute the heat of activation Q and the heat of desorption of ammonia less that of hydrogen, $\lambda_0-\lambda_1$, tabulated below. Q and $\lambda_0-\lambda_1$ are in calories per mol.

Catalyst.	Q.	$\lambda_0-\lambda_1$.
Used molybdenum (*a*):		
High temperature.....	24,500	500
Low temperature	60,200	500
New molybdenum (*b*):		
High temperature.....	26,050	800
Low temperature	44,900	800
Tungsten	41,500	—
Iron catalyst no. 1	45,800	13,000
Iron catalyst no. 2	41,600	5300

A break in the curves of fig. 4 for molybdenum, they interpret, determines a temperature (740° C.) above which any nitride ceases to exist in the presence of hydrogen.

They infer that the decomposition on the two iron catalysts may actually take place on nitrides formed from the nitrogen in the ammonia.

Bureau of Chemistry and Soils,
U. S. Department of Agriculture,
Washington, D. C.,
August 10th, 1929.

XCIV. *On some Integrals involving Legendre Polynomials.* *By* Dorothy Wrinch, *M.A.*, *D.Sc.*, *Hertha Ayrton Fellow*, *Girton College*, *Cambridge* *.

Introduction and Summary.

In the course of an investigation into the pressure on a spheroidal obstacle in the presence of a source of fluid at a point on its axis, it became necessary to evaluate the integral

$$\int_{-1}^{+1} \frac{\mu(1-\mu^2)}{\nu^2-\mu^2} \mathrm{P}_m'(\mu)\mathrm{P}_n'(\mu)\,d\mu$$

when ν^2 is greater than unity and m and n are positive integers. This integral, evidently zero when $m+n$ is even, at once directs attention when $m+n$ is odd to the integral

$$\tfrac{1}{2}\int_{-1}^{+1} (1-\mu^2)\mathrm{P}_m'(\mu)\mathrm{P}_n'(\mu)\frac{d\mu}{\nu-\mu},$$

to which it is then equal. Since the characteristic properties of the Legendre functions allow the product

$$(1-\mu^2)\mathrm{P}_m'(\mu)\mathrm{P}_n'(\mu)$$

to be expressed in the form

$$a_{m+n}\mathrm{P}_{m+n}(\mu) + a_{m+n-2}\mathrm{P}_{m+n-2}(\mu) + \ldots$$

with appropriate values of the constant coefficients, the key integral is

$$\tfrac{1}{2}\int_{-1}^{+1} \mathrm{P}_n(\mu)\frac{d\mu}{\nu-\mu}.$$

Now this integral has been shown by Neumann † to be equal to $\mathrm{Q}_n(\nu)$, when n is a positive integer, provided that

* Communicated by the Author.

† See Whittaker and Watson, 'Modern Analysis,' p. 320 (1927).

ν is not a real number between -1 and $+1$. In view of the recurrence relations possessed by the Legendre functions, an argument based on induction offered an elementary and yet elegant method of evaluation of the integral first required, since such a relation is in all cases involved when induction is used. It was found that by this method the evaluation of a wide class of integrals could readily be effected, and further, that the line of argument could be admirably demonstrated by evaluating the key integral. For this reason a proof of Neumann's result is first given.

On the basis of this result are quickly established the formulæ

$$\tfrac{1}{2}\int_{-1}^{+1} \mathrm{P}_n(\mu)\mathrm{P}_m(\mu)\frac{d\mu}{\nu-\mu} = \mathrm{P}_n(\nu)\mathrm{Q}_m(\nu), \qquad n \leq m\,;$$

$$\left.\begin{aligned} &\tfrac{1}{2}\int_{-1}^{+1} \mathrm{P}_n'(\mu)\mathrm{P}_m(\mu)\frac{d\mu}{\nu-\mu} \\ &\quad = \mathrm{P}_n'(\nu)\mathrm{Q}_m(\nu), && n \leq m+1 \\ &\quad = \mathrm{Q}_n'(\nu)\mathrm{P}_m(\nu) + \frac{1}{2}\left(\frac{1}{\nu-1} - \frac{(-1)^{n-m}}{\nu+1}\right), && n \geq m+1 \end{aligned}\right\};$$

$$\tfrac{1}{2}\int_{-1}^{+1} (\mu^2-1)\mathrm{P}_n'(\mu)\mathrm{P}_m'(\mu)\frac{d\mu}{\nu-\mu} = (\nu^2-1)\mathrm{P}_n'(\nu)\mathrm{Q}_m'(\nu), \quad n \leq m.$$

It should be remarked that it proves necessary only to exclude real values of ν between -1 and $+1$ and not (as in the application for which the original integral was first required) to make ν a real number such that ν^2 is greater than 1. By the adoption of a cross-cut in the ν-plane from -1 to $+1$, $\mathrm{Q}_m(\nu)$ becomes a one-valued function of ν.

§ 1. Let

$$a_n(\nu) = \tfrac{1}{2}\int_{-1}^{+1} \mathrm{P}_n(\mu)\frac{d\mu}{\nu-\mu},$$

$$a_n(\nu) = \tfrac{1}{2}\int_{-1}^{+1} \mu\mathrm{P}_n(\mu)\frac{d\mu}{\nu-\mu}.$$

Since the Legendre function $\mathrm{P}_n(z)$ (as also the associated function $\mathrm{Q}_n(z)$) satisfies the recurrence relation

$$(n+1)\chi_{n+1}(z) - (2n+1)z\chi_n(z) + n\chi_{n-1}(z) = 0, \quad . \quad (1)$$

it follows that

$$(n+1)a_{n+1}(z) - (2n+1)a_n(z) + na_{n-1}(z) = 0.$$

But so long as n is not zero,

$$\int_{-1}^{+1} P_n(\mu)\, d\mu = 0,$$

and therefore $a_n(\nu) = \nu\alpha_n(\nu)$. Hence, not only the two Legendre functions but also the function $\alpha_n(z)$ satisfies the recurrence relation.

Consider, now, the values of $\alpha_0(\nu)$ and $\alpha_1(\nu)$. We have

$$\alpha_0(\nu) = \tfrac{1}{2}\int_{-1}^{+1} \frac{d\mu}{\nu-\mu} = \tfrac{1}{2}\log\frac{\nu+1}{\nu-1} = Q_0(\nu),$$

$$\alpha_1(\nu) = \tfrac{1}{2}\int_{-1}^{+1} \mu\frac{d\mu}{\nu-\mu} = \nu Q_0(\nu) - 1 = Q_1(\nu),$$

and since the ν-plane is cut from -1 to $+1$, $Q_0(\nu)$ and $Q_1(\nu)$ are one-valued functions of ν. Thus $\alpha_n(\nu)$ is a function which is equal to the Legendre function $Q_n(\nu)$ when $n=0$ and when $n=1$, and shares with this function a recurrence relation of the second order. It follows that when n is an integer

$$\alpha_n(\nu) = Q_n(\nu), \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and that

$$a_n(\nu) = \nu Q_n(\nu) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

except in the case when n is zero, when $a_n(\nu) = Q_1(\nu)$.

§ 2. The next integrals to be discussed are

$$\beta_{n,m} = \tfrac{1}{2}\int_{-1}^{+1} P_n(\mu)P_m(\mu)\frac{d\mu}{\nu-\mu},$$

$$b_{n,m} = \tfrac{1}{2}\int_{-1}^{+1} \mu P_n(\mu)P_m(\mu)\frac{d\mu}{\nu-\mu}.$$

We have at once

$$\left.\begin{aligned} \nu\beta_{n,m}(\nu) - b_{n,m}(\nu) = \tfrac{1}{2}\int_{-1}^{+1} P_n(\mu)P_m(\mu)\, d\mu &= \frac{1}{2m+1}, \quad n=m \\ &= 0, \qquad\quad n\neq m \end{aligned}\right\}. \quad . \quad . \quad . \quad (4)$$

The application of the recurrence relation (1) to the function $P_n(\mu)$ in the integrand of $\beta_{n,m}(\nu)$ yields now the result that $\beta_{n,m}(z)$ *qua* function of n, also shares this recurrence relation for all values of n, with the one exception that when $n=m$ the relation becomes

$$(m+1)\beta_{m+1,m}(z) - (2m+1)z\beta_{m,m}(z) + m\beta_{m-1,m}(z) = -1. \quad (5)$$

But

$$\beta_{0,m}(\nu)=\alpha_m(\nu)=Q_m(\nu)=P_0(\nu)Q_m(\nu),$$

$$\beta_{1,m}(\nu)=a_m(\nu)=\nu Q_m(\nu)=P_1(\nu)Q_m(\nu).$$

The inductive argument establishes the result

$$\beta_{n,m}(\nu)=P_n(\nu)Q_m(\nu), \qquad n\leq m, \quad . \quad . \quad (6)$$

and from (4) we deduce

$$\left.\begin{aligned} b_{n,m}(\nu)&=\nu P_n(\nu)Q_m(\nu), && n<m\\ b_{m,m}(\nu)&=\nu P_m(\nu)Q_m(\nu)-1/(2m+1) \end{aligned}\right\}. \quad . \quad (7)$$

Since any polynomial of degree n can be expressed in the form

$$a_0P_0+a_1P_1+\ \dots\ +a_nP_n,$$

we have as an immediate corollary to (6) the theorem:

If $\phi(z)$ is any polynomial of degree not greater than m, then

$$\tfrac{1}{2}\int_{-1}^{+1}\phi(\mu)P_m(\mu)\frac{d\mu}{\nu-\mu}=\phi(\nu)Q_m(\nu).$$

§ 3. Since $\beta_{n,m}(\nu)$ and $b_{n,m}(\nu)$ are functions symmetric in the two parameters m and n, it is not necessary to attempt an independent evaluation when n is greater than m. However, for the sake of studying this type of argument, it is worth while to exhibit the fashion in which the interchange of the P and Q functions is accomplished.

Since for $n>m$ as for $n<m$ the function $\beta_{n,m}(z)$ satisfies the recurrence relation (1), the equality

$$\beta_{n,m}(\nu)=Q_n(\nu)P_m(\nu), \qquad n\geq m \quad . \quad . \quad (8)$$

at once follows if it is true for $n=m$ and for $n=m+1$. Now when $n=m$ the recurrence relation established for $\beta_{n,m}(\nu)$ takes the special form (5), and the values of $\beta_{n,m}(\nu)$ for $n=m-1$ and $n=m$ already found yield the consequence that

$$\beta_{m+1,m}(\nu)=P_{m+1}(\nu)Q_m(\nu)-1/(m+1).$$

But, as is well known,

$$P_{m+1}(\nu)Q_m(\nu)-Q_{m+1}(\nu)P_m(\nu)=1/(m+1).$$

Hence the result (8), established for $n=m$ as a case of (6), is now established for $n=m+1$ and so for all larger values of n.

For the function $b_{n,m}(\nu)$ the corresponding result

$$b_{n,m}(\nu)=\nu Q_n(\nu)P_m(\nu), \qquad n>m, \quad . \quad (9)$$

can now be based on (4) instead of being inferred by symmetry from (7).

§ 4. We consider next the integrals

$$\gamma_{n,m}(\nu)=\int_{-1}^{+1} P_n'(\mu)P_m(\mu)\frac{d\mu}{\nu-\mu},$$

$$c_{n,m}(\nu)=\int_{-1}^{+1} \mu P_n'(\mu)P_m(\mu)\frac{d\mu}{\nu-\mu}.$$

The derivative $P_n'(z)$ being a polynomial of degree $n-1$, these integrals come, the former for $n\leq m+1$ and the latter for $n\leq m$, within the theorem at the close of § 2, and we have

$$\gamma_{n,m}(\nu)=P_n'(\nu)Q_m(\nu), \qquad n\leq m+1, \quad (10)$$

$$c_{n,m}(\nu)=\nu P_n'(\nu)Q_m(\nu), \qquad n\leq m. \quad . \quad (11)$$

To evaluate the first integral when n takes larger values, we use the relation

$$\chi'_{n+1}(z)-\chi'_{n-1}(z)=(2n+1)\chi_n(z),$$

which is true for $P_n(z)$ and $Q_n(z)$. Because this relation is true for $P_n(z)$,

$$\begin{aligned}\gamma_{n+1,m}(\nu)-\gamma_{n-1,m}(\nu)&=(2n+1)\beta_{n,m}(\nu)\\&=(2n+1)Q_n(\nu)P_m(\nu), \qquad n\geq m,\end{aligned}$$

and because the same relation is true for $Q_n(z)$,

$$(2n+1)Q_n(\nu)P_m(\nu)=Q'_{n+1}(\nu)P_m(\nu)-Q'_{n-1}(\nu)P_m(\nu).$$

Thus for $n\geq m$,

$$\gamma_{n+1,m}(\nu)-Q'_{n+1}(\nu)P_m(\nu)=\gamma_{n-1,m}(\nu)-Q'_{n-1}(\nu)P_m(\nu),$$

and therefore, for $n=m+2,\ m+4,\ m+6,\ \ldots$,

$$\begin{aligned}\gamma_{n,m}(\nu)-Q_n'(\nu)P_m(\nu)&=\gamma_{m,m}(\nu)-Q_m'(\nu)P_m(\nu)\\&=P_m'(\nu)Q_m(\nu)-Q_m'(\nu)P_m(\nu)\\&=1/(\nu^2-1),\end{aligned}$$

and for $n=m+3,\ m+5,\ m+7,\ \ldots$,

$$\begin{aligned}\gamma_{n,m}(\nu)-Q_n'(\nu)P_m(\nu)&=\gamma_{m+1,m}(\nu)-Q_{m+1}'(\nu)P_m(\nu)\\&=P_{m+1}'(\nu)Q_m(\nu)-Q_{m+1}'(\nu)P_m(\nu)\\&=\nu/(\nu^2-1).\end{aligned}$$

That is, for $n > m$,

$$\left.\begin{aligned}\gamma_{n,m}(\nu) &= Q_n'(\nu)P_m(\nu) + 1/(\nu^2-1), \quad n-m \text{ even}\\ &= Q_n'(\nu)P_m(\nu) + \nu/(\nu^2-1), \quad n-m \text{ odd}\end{aligned}\right\}, \quad (12)$$

and the results for $\gamma_{n,m}(\nu)$ may be stated as follows:

$$\left.\begin{aligned}\gamma_{n,m}(\nu) &= P_n'(\nu)Q_m(\nu), && n \leq m+1\\ &= Q_n'(\nu)P_m(\nu) + \frac{1}{2}\left(\frac{1}{\nu-1} - \frac{(-1)^{n-m}}{\nu+1}\right), && n \geq m+1\end{aligned}\right\}. \quad . \quad . \quad . \quad (13)$$

To complete the evaluation of $c_{n,m}(\nu)$, we notice that for $n > m$

$$\left.\begin{aligned}\nu\gamma_{n,m}(\nu) - c_{n,m}(\nu) &= \tfrac{1}{2}\int_{-1}^{+1} P_n'(\mu)P_m(\mu)\,d\mu = 0, \quad n-m \text{ even}\\ &= 1, \quad n-m \text{ odd}\end{aligned}\right\},$$

whence

$$\left.\begin{aligned}c_{n,m}(\nu) &= \nu Q_n'(\nu)P_m(\nu) + \nu/(\nu^2-1), \quad n-m \text{ even}\\ &= \nu Q_n'(\nu)P_m(\nu) + 1/(\nu^2-1), \quad n-m \text{ odd}\end{aligned}\right\}, \quad (14)$$

and the results corresponding to (13) run

$$\left.\begin{aligned}c_{n,m}(\nu) &= \nu P_n'(\nu)Q_m(\nu), && n \leq m\\ &= \nu Q_n'(\nu)P_m(\nu) + \frac{1}{2}\left(\frac{1}{\nu-1} + \frac{(-1)^{n-m}}{\nu+1}\right), && n \geq m\end{aligned}\right\}. \quad . \quad . \quad . \quad (15)$$

§ 5. The evaluation of the original integral

$$\delta_{n,m}(\nu) = \tfrac{1}{2}\int_{-1}^{+1} (\mu^2-1)P_n'(\mu)P_m'(\mu)\frac{d\mu}{\nu-\mu}$$

may now be completed. Both $P_m(z)$ and $Q_m(z)$ satisfy the relation

$$(z^2-1)\chi_m'(z) = mz\chi_m(z) - m\chi_{m-1}(z).$$

Hence

$$\delta_{n,m}(\nu) = m\{c_{n,m}(\nu) - \gamma_{n,m-1}(\nu)\}, \quad . \quad . \quad . \quad (16)$$

and for $n \leq m$,

$$\begin{aligned}\delta_{n,m}(\nu) &= mP_n'(\nu)\{\nu Q_m(\nu) - Q_{m-1}(\nu)\}\\ &= (\nu^2-1)P_n'(\nu)Q_m'(\nu). \quad . \quad . \quad . \quad . \quad (17)\end{aligned}$$

By symmetry we have for $n \geq m$,

$$\delta_{n,m}(\nu) = (\nu^2-1)Q_n'(\nu)P_m'(\nu)\ ; \quad . \quad . \quad . \quad (18)$$

it is not necessary to discuss this case, but a glance will verify that the result is deducible alternatively by the application of (12) and (14) to (16).

Finally, it may be recorded that, since

$$\tfrac{1}{2}\int_{-1}^{+1}(\mu^2-1)\mathrm{P}_n'(\mu)\mathrm{P}_m'(\mu)\frac{d\mu}{\nu+\mu}=(-)^{m+n}\delta_{n,m}(\nu),$$

we have, if $n \leq m$,

$$\tfrac{1}{2}\int_{-1}^{+1}\mu\frac{\mu^2-1}{\nu^2-\mu^2}\mathrm{P}_n'(\mu)\mathrm{P}_m'(\mu)\,d\mu=(\nu^2-1)\mathrm{P}_n'(\nu)\mathrm{Q}_m'(\nu), \quad (19)$$
$$m+n \text{ odd},$$

$$\tfrac{1}{2}\int_{-1}^{+1}\nu\frac{\mu^2-1}{\nu^2-\mu^2}\mathrm{P}_n'(\mu)\mathrm{P}_m'(\mu)\,d\mu=(\nu^2-1)\mathrm{P}_n'(\nu)\mathrm{Q}_m'(\nu), \quad (20)$$
$$m+n \text{ even},$$

whereas the former of these integrals is zero if $m+n$ is even, as was remarked at the outset, and the latter is zero if $m+n$ is odd.

XCV. *On the Elastic Extension of Metal Wires under Longitudinal Stress.*—Part I. *A New Method for Measuring the Deviation from Hooke's Law.* *By* L. C. Tyte, *B.Sc., A.Inst.P., Research Student, East London College**.

Introduction.

THE object of the experiments was to examine the departure from Hooke's law when a wire was subjected to longitudinal stress, a method being devised by Professor Lees by which the deviation was obtained directly.

The principle of the method was to determine the difference between the extensions of two wires, of the same cross-sectional area and of the same material, one double the length of the other, the stretching force on the shorter being double that on the longer. If Hooke's law were strictly true both wires would extend by equal amounts, but any deviation from the law would cause one wire to extend more than the other, the excess being measured by the tilt of an optical lever.

Description of Apparatus.

A diagram of the apparatus is shown in fig. 1. A steel bar A was screwed on to a stout wooden beam supported

* Communicated by Prof. C. H. Lees, F.R.S.

between two iron girders. The bar was fitted at either end with steel lugs B, brazed on to the opposite edges of the bar in such a manner that the horizontal planes passing through their upper surfaces were one metre apart. Holes were drilled in these lugs to accommodate the metal chucks C (fig. 2). These chucks had a fine hole drilled along the axis

Fig. 1.

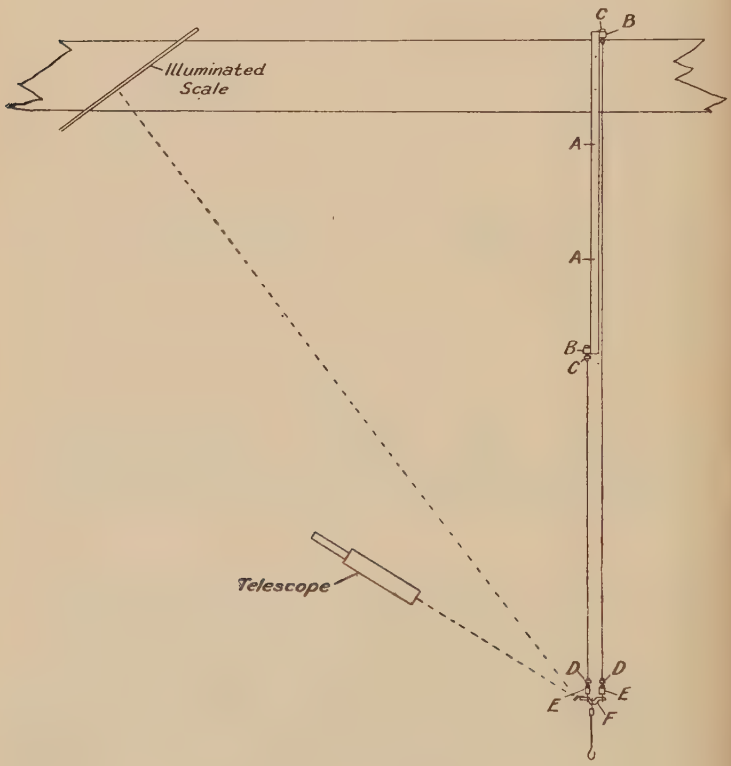
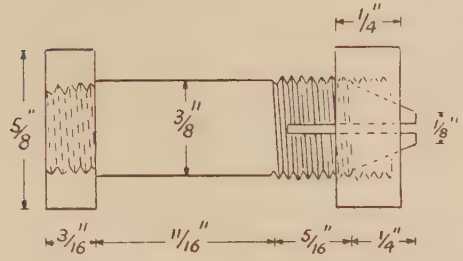


Diagram of Apparatus.

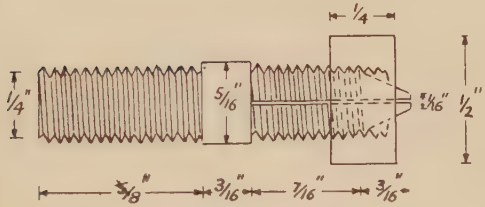
to accommodate the experimental wire, and one end was tapered, threaded, split with an axial saw-cut, and provided with a screw nut, thus gripping the wire, the other end being fitted with a nut to stop the chuck slipping through the hole in the lug. The lower ends of the wires supported chucks D (fig. 3), one end of which gripped the wire, and the other was fitted with a simple thread, on which the stirrup-shaped pieces E (shown in fig. 4) could be screwed.

Fig. 2.



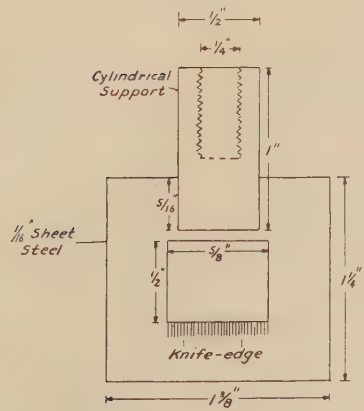
Upper Chucks.

Fig. 3.



Lower Chucks.

Fig. 4.



Steel Stirrup Piece.

The aluminium ones were somewhat smaller and had a steel knife-edge set in the lower inner edge.

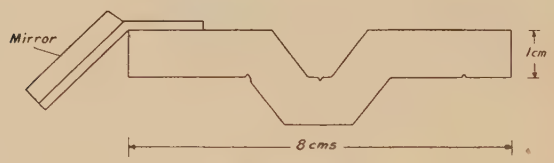
The lower inner edges of these stirrups formed knife-edges, on which rested a cranked bar F (fig. 5). This bar was provided with three V-shaped notches—one, in the centre of the bar, on the upper surface of the cranked portion, two on the lower surface of the bar, on opposite sides of the centre, and 1·5 cm. and 3·0 cm. respectively from it.

The knife-edges attached to the wires rested in the two outer notches, while a third stirrup-shaped piece fitted into the centre notch and supported the load.

Two ratio-bars and two sets of stirrups were used, a steel ratio-bar and stirrups for wires of high tensile strength, and an aluminium set for materials of small tensile strength. Two sets of chucks were also used, one set made of steel for the steel wires, and one of brass for the other materials.

The wires used were 1 and 2 metres long respectively, with their lower ends at the same level. At the commencement of an experiment, with sufficient load on the wires to

Fig. 5.



Steel Ratio-bar.

The aluminium one was exactly similar, but only 0·6 cm. square instead of 1 cm.

keep them taut, the ratio-bar was horizontal, any slight tilt being removed by screwing one of the knife-edges up or down. The ratio-bar ensures that any load put on it is divided in the ratio of 2 : 1 between the shorter and longer wires. Any inequality in the extensions will result in a tilt of the ratio-bar, measured by a beam of light reflected from a small mirror attached to the end of the ratio-bar on the side of the shorter wire. Light from a fixed illuminated scale about 240 cm. away from the mirror, and perpendicular to the line joining its zero-point to the mirror, is reflected from the mirror into an observing telescope.

It was found that the system swung too much for observations to be taken unless the motion was restricted by passing the cylindrical portions of the stirrups through two holes bored in a sheet of aluminium, which was placed so that the centres of the holes were accurately under the upper

chucks. The stirrups fitted loosely in the holes and were kept well oiled, so that frictional loss was negligible.

Calculation of the Constant of the Apparatus.

If ϵ is the excess extension of one of the wires, tilting the ratio-bar through an angle ϕ, and d the distance between the wires, *i.e.*, the outer knife-edges, then

$$\epsilon/d = \tan\phi = \phi,$$

assuming ϕ to be small.

Similarly, if λ is the distance of the illuminated scale from the mirror, and D is the scale reading deflexion given by the excess extension ϵ,

$$D/\lambda = \tan 2\phi = 2\phi.$$

Thus

$$\epsilon = Dd/2\lambda, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$d/2\lambda$ being the constant of the apparatus; λ depends on the set of chucks used, and d on the ratio-bar. The mean values of the measurements of the distance λ and of the lengths of the arms of the ratio-bars are given in the following table:—

	Mean distance from mirror to scale.	Mean length of short ratio-arm.	Mean length of long ratio-arm.	Ratio.	Total distance between wires.
	cm.	cm.	cm.		cm.
Steel set.....	242·9	1·510	3·0125	1·995 : 1·000	4·5225
Aluminium set.	242·3	1·509	3·019	2·0007 : 1·000	4·528

The values of the constants of the apparatus are 0·009308 and 0·009344 for the steel and aluminium sets respectively. Hence, as the scale readings can be read to 0·01 cm., the apparatus is capable of measuring differences in the extensions of the two wires to less than 1 part in 10^6.

Discussion of Possible Sources of Error.

1. *Slip of the Wires through the Chucks.*—The agreement of the readings shows that this did not occur to a measurable extent.

2. *Error of Ratio in the Ratio-bar.*—Assume that the ratio of the lengths of the wires and of the arms of the ratio-bar should be in the ratio $a:1$, but that an error in the latter case makes the ratio $a(1+\delta):1$. Hence, if L and b are the lengths of the shorter wire and ratio-arm respectively, a load M on the ratio-bar is divided into forces

$$a(1+\delta)\mathrm{M}/[1+a(1+\delta)] \quad \text{and} \quad \mathrm{M}/[1+a(1+\delta)],$$

causing extensions

$$e_1=\mathrm{L}a(1+\delta)\mathrm{M}/\mathrm{E}_1\mathrm{A}[1+a(1+\delta)]$$

and

$$e_2=\mathrm{L}a\mathrm{M}/\mathrm{E}_2\mathrm{A}[1+a(1+\delta)]$$

of the shorter and longer wires respectively, where E_1 and E_2 are the values of Young's Modulus corresponding to the stress conditions, and A the cross-sectional area of the wires. Therefore

$$e_1/e_2=[(1+\delta)\mathrm{E}_2]/\mathrm{E}_1,$$

and the difference ot extensions caused by the error in the ratio-bar is

$$e_1-e_2=[\{(1+\delta)\mathrm{E}_2\}/\mathrm{E}_1-1]e_2.$$

Hence

$$\tan\phi_{\text{Expt.}}=[\{(1+\delta)\mathrm{E}_2\}/\mathrm{E}_1-1]e_2/b[1+a(1+\delta)], \quad (2)$$

and

$$\tan\phi_{\text{Theory}}=[\mathrm{E}_2/\mathrm{E}_1-1]e_2/b[1+a]\ ; \quad . \quad . \quad (3)$$

$$\therefore \quad \tan(\phi_{\text{Expt.}}-\phi_{\text{Theory}})=$$

$$\frac{\dfrac{[\{(1+\delta)\mathrm{E}_2\}/\mathrm{E}_1-1]e_2}{b[1+a(1+\delta)]}-\dfrac{[\mathrm{E}_2/\mathrm{E}_1-1]e_2}{b[1+a]}}{1+\dfrac{[\{(1+\delta)\mathrm{E}_2\}/\mathrm{E}_1-1][\mathrm{E}_2/\mathrm{E}_1-1]e_2^2}{b^2[1+a(1+\delta)][1+a]}},$$

which, neglecting the e_2^2 term, reduces to

$$e_2\delta[\mathrm{E}_2/\mathrm{E}_1+a]/b(1+a)[1+a(1+\delta)]\ ;$$

further, assuming Hooke's law to hold for consideration of this error,

$$\tan(\phi_{\text{Expt.}}-\phi_{\text{Theory}})=e_2\delta/b[1+a(1+\delta)], \quad . \quad . \quad (4)$$

and the actual error of excess extension causing it is $e_2\delta$, which is proportional to the load.

From the table, $\delta_{\text{Steel}}=-0{\cdot}0025$ and $\delta_{\text{Aluminium}}=+0{\cdot}00035$, which means errors of $-0{\cdot}25$ per cent. and $+0{\cdot}35$ per cent. respectively {considering errors which increase the excess

extension of the shorter wire over the longer to be positive} of the Hooke's law extensions of the wires. Hence from equation (2) it is seen that for δ negative the value of $\tan \phi_{\text{Expt.}}$ starts by being negative, increases to a maximum value, then falls to zero and becomes positive, the maximum and zero values depending on the rate of increase of E_2/E_1 and δ.

The percentage error of the error with respect to the excess extension is given by

$$[\delta/[\{(1+\delta)E_2\}/E_1-1]] \times 100 \text{ per cent.}$$

This, in the case of the steel bar, starts as being negative, and rapidly increases until the denominator is zero, when it changes sign and is a large positive quantity, which rapidly decreases. From the results it appears that this change of sign of the error occurs for very small stresses. In the other case, with δ positive, it steadily decreases throughout.

3. *Error due to Knife-edges not being in the same Plane.*—Suppose that the three knife-edges are not in the same plane, but that the centre one is lower than the other two, thus forming the corners of a triangle ABC. Drop a perpendicular from C to AB at D, and call the distances AD, DB, and CD, b, $2b$, and x respectively. When the ratio-bar is in its normal untilted position, the ratio of the arms is $2b : b$, but if it is deflected through a small angle θ the ratio becomes

$$2b - x\tan\theta : b + x\tan\theta,$$

or

$$2\{1-\frac{x}{2b}\tan\theta\}/\{1+\frac{x}{b}\tan\theta\} : 1,$$

which can be written

$$2\{1-\frac{x}{2b}\tan\theta\}\{1-\frac{x}{b}\tan\theta\} : 1$$

as a first approximation, reducing to

$$2\{1-\frac{3x}{2b}\tan\theta\} : 1.$$

For the steel ratio-bar $x = 0{\cdot}10$ cm., and for the aluminium bar $x = 0{\cdot}62$ cm.; b can be assumed to equal 1·5 cm. for both cases. Hence the ratio for the steel bar is

$$2\{1-0{\cdot}1\tan\theta\} : 1,$$

and for the aluminium one

$$2\{1-0{\cdot}6\tan\theta\} : 1.$$

When the ratio-bar is tilted, owing to the excess extension of the shorter wire the ratio of the lengths of the arms is changed, and consequently the shorter wire receives a greater load, which increases the total extension of the wire. θ is a function of the load, and for the largest loads considered only amounts to 1°. Thus for the extreme cases the values of the ratio only become

1·9965 : 1 for steel, and

1·9790 : 1 for aluminium.

4. *Error in the Ratio of the Lengths of the Wires.*—Assuming Hooke's law for the consideration of this error, the error of the excess extension is proportional to the load, being positive if the shorter wire is more than half the longer and negative if less. Such an error would be small, for an error of 0·1 cm. in the length of the shorter wire makes a difference of 1 in 2000 in the ratio, and the error is more probably only a tenth of this. Further, there is no reason to believe that the error would always be in the same direction, and in the mean value it would largely cancel itself out.

5. *Error caused by Variation of the Distance from the Mirror to the Scale due to Extension of the Wires.*—When the wires extend they carry the mirror with them and increase the distance between the mirror and the illuminated scale. The actual excess extension of the wire ϵ and the observed scale deflexion D are connected by the relation

$$D = 2\lambda\epsilon/d ;$$

thus an increase in the value of λ makes the observed deflexion larger than it should be. λ is approximately 242 cm., and the greatest value of the total extension is 0·7 cm., being usually less than a tenth of this, and since the illuminated scale is inclined at an angle of 35° to the horizontal, the actual increase in λ is 0·7 cos 35° or 0·57 cm. Therefore the error would be

$$\{0{\cdot}57 \times 100/242\} \text{ per cent.} = \tfrac{1}{4} \text{ per cent. approx.}$$

This is not an error affecting the total extension of the wire, but merely an error of observation in the determination of the actual excess extension.

6. *Error in the Assumption that* $\tan\phi \equiv \phi$ *and* $\tan 2\phi \equiv 2\phi$.—The important assumption is that $\tan 2\phi \equiv 2\phi$, for this includes the other. Now

$$\tan 2\phi = D/\lambda ;$$

the largest deflexion observed was $D = 5$ cm., and $\lambda = 242$ cm. Thus

$$\tan 2\phi = 5/242 = 0{\cdot}0207,$$

and

$$2\phi = 1^\circ\ 11'.$$

The value of $1^\circ\ 11'$ in radians is 0·0207 ; and hence the assumption is perfectly justified within the limits of the experiments.

7. *Error due to the Initial Loads on the Wires not being in the Correct Ratio.*—If the initial loads, caused by the chucks and ratio-bar, on the two wires are not in the correct ratio, an error is introduced. In the case of the steel ratio-bar and accessories (with one exception) the load on the shorter wire was 152·6 gm., and that on the longer wire 68·7 gm. Thus there was a load of approximately 15 gm. too much on the shorter wire; but as the initial load in these cases was 1 kilogramme, this was only a very small error. For the aluminium ratio-bar and accessories the ratio between the loads was made exact by attaching a small piece of lead to the stirrup piece attached to the longer wire.

8. *Error due to Expansion of the Wires caused by Variations of the Room-temperature.*—The usual difficulties caused by the expansion of the experimental wire are eliminated by the use of two wires, but a new source of error is introduced when the material under examination has a coefficient of expansion different from that of the steel supporting bar. Then temperature fluctuations will cause differential expansion between the metre of steel supporting bar and one metre of the test wire. The values of these errors are only quite small, being negligible for steel, iron, and nickel, approximately 6×10^{-4} cm. per degree C. for copper and brass, and approximately 14×10^{-4} cm. per degree C. for aluminium, zinc, tin, and lead.

The experiments were performed in a basement laboratory, the temperature variations of which were small, the complete fluctuation for a day being usually less than a degree. Further, the change would sometimes be an increase and sometimes a decrease in temperature, and this source of error would tend to cancel out in the mean value.

Discussion of Method.

This new method can claim many advantages, among which are the simplicity of design and manipulation, being quite free from mechanical devices introducing undesirable frictional forces.

To investigate deviations from Hooke's law for wires by the ordinary extension method specimens of 10 to 20 metres length are required; hence the present apparatus possesses the advantage of compactness and convenience for use in the ordinary laboratory, and requires much less material, which means greater uniformity over the specimen. Further, the sensitiveness, which in the present apparatus is 1 part in 10^6 in the excess extension, can be pushed to almost any limit by decreasing the length of the lever arm, *i.e.*, the distance between the wires, and increasing the optical path between the mirror and scale, thus surpassing as an instrument of precision the interference method due to Grüneisen. The chief disadvantage is that the actual extension of the specimens is not known, but it is hoped to construct a new extensometer capable of giving simultaneous observations of the extension and excess extension.

Conclusion.

The instrument has been found to behave perfectly satisfactorily in use, and observations have been made on a large number of metals. The results of these investigations are to be published in a subsequent paper.

XCVI. *The Comparison of Molecular Ionizing Potentials in an Alternating Electric Wind.* *By* W. M. Thornton, *D.Sc., D.Eng., Armstrong College, Newcastle-on-Tyne* *.

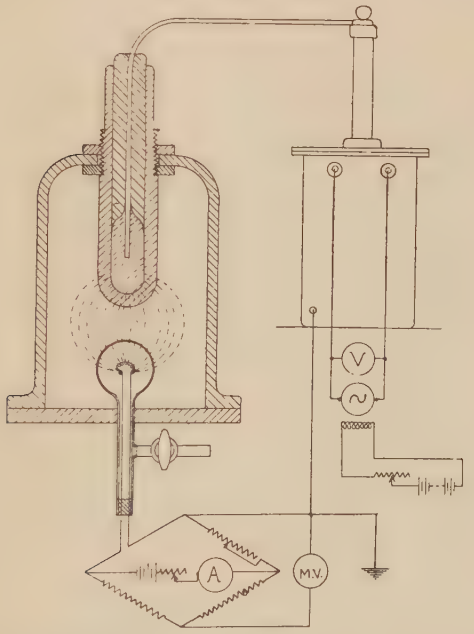
1. Introduction.

THE intensity of the electric wind from a pole of a strong alternating field is proportional both to the velocity of molecular ions and to their number. When one pole is earthed there is still a wind to be observed from it, for the effect depends on the local gradient, not on the total voltage alone. If this earthed pole is made a hot wire the wind is much increased, and its cooling influence can be so great that a red-hot wire is reduced by it to blackness. This cooling is a linear function of the field over a wide range, and since the velocity of ions in gases at atmospheric pressure is proportional to the field, the number of ions is also proportional to it. By enclosing the hot wire in an insulating vessel, fig. 1, containing a gas at pressures from

* Communicated by the Author.

10 cm. of mercury to atmospheric pressure, and insulating the high tension electrode, the other end of the secondary winding being earthed, the arrangement provides a new means of observing the behaviour of a gas in a strong electric field with only one electrode in the gas. This has certain advantages. High voltages can be used without risk of shock or electrical breakdown, and the wire being at earth potential can be made part of a bridge by which its change of resistance may be continuously observed.

Fig. 1.



The galvanometer deflexion of a bridge of which the hot wire is one arm is at the start proportional to the field, so that the steepest tangent drawn to the curves connecting deflexion and applied field voltage is a measure of the molecular ionization produced. For a given apparatus the product of maximum slope of curve and ionizing potential should therefore be approximately constant. This is shown below to be the case by the behaviour of the monatomic gases helium, neon, and argon. The slope of the observed curve for argon in a particular apparatus was 0·0133 bridge volts per volt of field, its ionizing potential is

11·5. The product of these is 0·153. Dividing this number by the slope of the curve for any other gas in the same apparatus gives a measure of its molecular ionizing potential, which should be inversely proportional to the tangent to the curve, and the following ionizing potentials of gases were found in this way. It is given as a new and convenient method of comparing ionization by which no current is passed *through* the gas, the ions being forced to move to and fro as the field reverses, the alternating molecular movement cooling the hot wire which forms the earthed pole.

2. Monatomic Gases.

The gases helium, neon, and argon have first ionizing potentials of 25·4, 21·5, and 11·5 volts respectively. These are sufficiently distinct to provide a test of the nature of the wind and of the validity of the method by finding whether the cooling of the wire in the three gases under the influence of an electric field is inversely proportional to these potentials. The tube enclosing the gas and the wire was placed near to an insulated high tension electrode, the other pole being the wire itself. The voltages given as abscissæ are those applied between the two electrodes, the hot wire being earthed. A simple bridge method was used, the initial current in the hot-wire circuit being constant at 0·4 ampere throughout. The gases were transferred by mercury displacement from the bulbs in which they were supplied by the British Oxygen Co., but not further dried, direct to the test vessel at a pressure of 10 centimetres of mercury.

Argon (I. P. 11·5 volts).

(Argon 99 per cent., nitrogen 0·7 per cent., oxygen 0·3 per cent.)

On the application of the field there was in the apparatus used no cooling of the wire until a voltage of 24 kV. had been reached. The slope of the curve, fig. 2, is 0·01328 bridge volts per volt. The product of slope and ionizing potential is 0·1530.

Neon (I. P. 21·5 volts).

(Neon 98 per cent., helium 2 per cent.)

Cooling started at 30 kV. Slope of curve 0·0080. The ionizing potential derived from the slope is 19·2.

Helium (I. P. 25·4 volts).

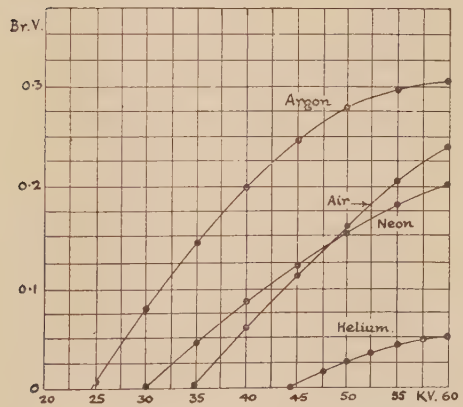
(Helium 98 per cent., neon 2 per cent.)

Starting voltage 45 kV. Slope of curve ·0057. Derived ionizing potential 26·8.

From these we have :

	Ionizing Potential, P.	Slope of Curve, S.	P.×S.
Argon	11·5	0·01328	0·1530
Neon	21·5	0·0080	0·1720
Helium	25·4	0·0057	0·1445
		Mean ..	0·1565

Fig. 2.



Argon was taken as the standard gas for comparison in the tests on other gases.

The cooling effect of the wind therefore follows the same sequence as the reciprocals of the ionizing potentials. There is greater cooling in argon in a given field because of its lower ionizing potential. Having regard to the early state of the knowledge of the effect and to its possible dependence on the chemical purity of the gases, the above agreement may be considered satisfactory. It is only by extended trials that the degree of precision possible can be found, but the results given below show that the effect is regular and consistent. The behaviour of mixtures of gases will be given in a later paper.

3. Diatomic Gases.

Hydrogen.

Working at the same current 0·4 ampere in the wire the normal cooling was so great that that due to the field was not perceptible up to 50 kV. The temperature was therefore raised and the out-of-balance volts measured, while the field was maintained constant at 50 kilovolts. The results are given in Table I.

There is a rapid rise in the rate of cooling of the wire by the field as the temperature approaches redness. It reaches a sharp maximum at 1·0 ampere, after which corona begins and the maximum of cooling falls. The

Table I.

Hydrogen at 10 cm. Hg pressure.

Current in wire. Amperes.	Out-of-balance volts due to constant field.
0·5	0·00
0·6	0·006
0·7	0·02
0·8	0·04
0·9	0·07
1·0	0·074
1·03	0·055 unsteady.

surface conditions are in any case completely modified by corona when it occurs.

The curves of fig. 3 have all nearly the same initial slope of 0·00364 bridge volts per volt applied. The ionizing potential of molecular hydrogen is not a fixed quantity, but taking for comparison the products of the slope and ionizing potential for argon

$$(\text{M. I. P.}) \times \cdot 0036 = 11 \cdot 5 \times \cdot 0133,$$

the value obtained for hydrogen $= 42 \cdot 4$.

Oxygen.

The observed slope of the curve given in fig. 4 for oxygen was 0·0220, which corresponds to $\cdot 153/\cdot 0220 = 6 \cdot 9$ volts for the molecular ionizing potential, the atomic potential being 13·56, or double the molecular value.

Fig. 3.

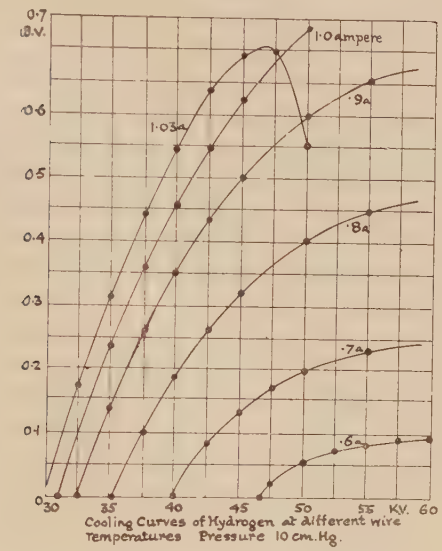
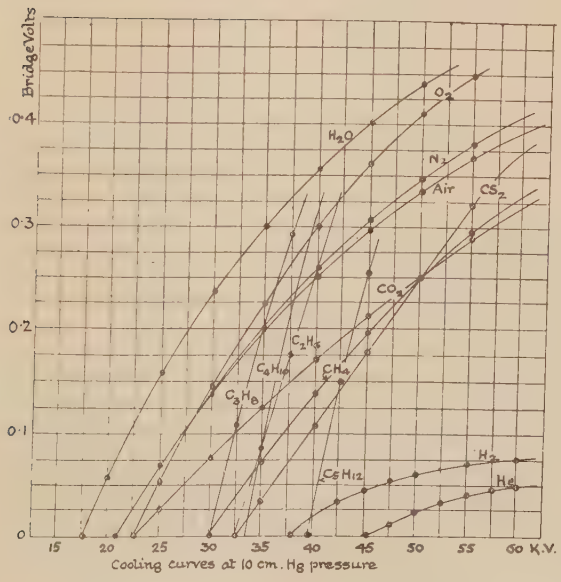

0·7
B.V.
0·6
0·5
0·4
0·3
0·2
0·1
0
1·0 Ampere
·9A
1·03A
·8A
·7A
·6A
30
35
40
45
50
55 KV. 60
Cooling Curves of Hydrogen at different wire
Temperatures Pressure 10 cm. Hg.

Fig. 4.


Bridge Volts
0·4
0·3
0·2
0·1
0
O2
H2O
N2
Air
CS2
CO2
C2H5
C4H10
CH4
C3H8
C5H12
H2
He
15
20
25
30
35
40
45
50
55
60 K.V.
Cooling curves at 10 cm. Hg pressure

Nitrogen.

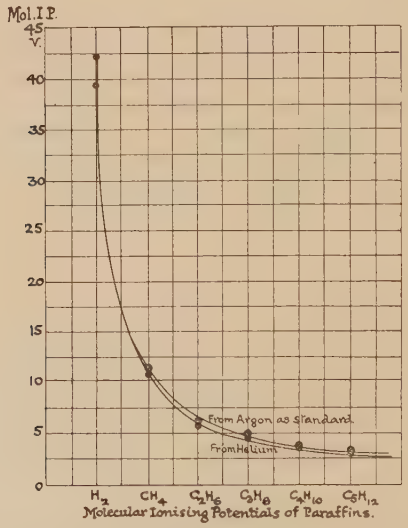
Observed slope 0·0133, corresponding to 0·153/·0133 =11·5, the atomic potential being 14·49.

Air.

Observed slope 0·0133, molecular potential 11·50. Air was identical with nitrogen and argon in the cooling effect of the wind on a hot wire. It is remarkable that these three gases in air should have the same molecular ionizing potentials.

In hydrogen it will be noted that the M. I. potential as

Fig. 5.



interpreted here is much higher than the atomic. In oxygen and nitrogen it is less.

4. The Paraffin Series.

The paraffin series of polyatomic gases is of special interest in engineering, methane being the most important factor in coal mining, and the higher members in internal combustion engines. It is the only regular series of gases available in convenient form. The methane was nearly pure, but contained a trace of nitrogen. Ethane was prepared from ethyl iodide by the zinc-copper couple, and passed through alcohol and strong sulphuric acid. Pro-

pane and butane were obtained from the Shell-Mex laboratories by the kindness of Mr. Kewley. Pentane was prepared from pure Karlbaum liquid. The molecular ionizing potentials were calculated in each case by dividing the product 0·153 of the slope and potential for argon by the observed slope of cooling of the wire in the gas under the action of the field.

The results gave for the ionizing potentials : methane 11·3 volts, ethane 6·32, propane 5, butane 3·77, pentane 3·49. These are shown in fig. 5 to form a regular curve with the number of methyl radicles or of carbon atoms as abscissæ. Its equation can be made to include hydrogen by writing it

$$(m-a)(n+b)=c,$$

where $a=0{\cdot}44$, $b=0{\cdot}326$, $c=14{\cdot}4$, m is the M. I. P., and n the number of carbon atoms.

The observed and calculated values are given below.

TABLE II.

	n.	m.	
		Obs.	Cal.
Hydrogen	0	42·4	43·8
Methane	1	11·3	11·29
Ethane	2	6·32	6·70
Propane.....	3	5·0	4·91
Butane	4	3·77	3·77
Pentane.....	5	3·49	3·14

The regularity of these figures supports the use of the method as an indicator of the behaviour of gases under electrification.

The results in Table II. are of interest in connexion with the suggestion that the ignition of gases and the propagation of flame might depend on ionization from the wave front or source. Ignition by unidirectional break-sparks * of mixtures of the paraffins of maximum inflammability requires the same igniting current for each gas in the series. In the case of alternating currents † tested by the same method it actually becomes *more difficult* to ignite the higher paraffins by break-sparks of this kind, although the heat of combustion of the gas is so much greater. But the

* "The Electrical Ignition of Gases," Proc. Roy. Soc. A, xc. fig. 2, p. 277 (1914).

† *Loc. cit.* fig. 12, p. 290.

present results show that ionization of the kind which might be expected in explosion—that is, molecular—takes less energy in the higher paraffins. There is no type of ignition of gases that becomes easier in the higher paraffins except that by hot wires. It is therefore improbable that molecular ionization such as is caused by collision of ions with molecules in an electric field plays any part in ignition, but that the whole effect is due to activation by radiation *.

The special interest of fig. 5 is that each addition of a CH_2 radicle lessens the energy required for ionization by collision in an electric field in a regular manner. Hydrogen itself has a high value, yet as the number of hydrogen atoms in the molecule is increased the critical ionizing potential diminishes. The presence of carbon atoms lowers the ionizing potential in close proportion to their number. The lower curve in fig. 5 is calculated from helium as a standard gas ; the difference is small.

5. Other Gases.

In order to examine the relative influence of carbon and hydrogen atoms on the effect, acetylene and ethylene were tested under the same conditions as before, with the following results :—

	Slope of Curve.	M. I. Pot.
Acetylene, C_2H_2	0·0243	6·29 volt.
Ethylene, C_2H_4	0·0245	6·25 ,,
Ethane, C_2H_6	0·0242	6·32 ,,

There is therefore evidence that the carbon atoms have a preponderating influence in ionization of hydrocarbons in strong fields. The influence of hydrogen would seem to be by comparison almost negligible, and it may be noted that the " atomic " ionizing potentials of ethane, acetylene, and ethylene are so nearly twice the present observed values of the molecular potentials. The ratios are 2·025, 1·96, 1·95 respectively.

The atomic ionizing potential of carbon is 11·3, not much different from atomic hydrogen (13·53), but molecular hydrogen is difficult to ionize in this manner.

Replacing three hydrogen atoms by chlorine, we have

	Slope.	M. I. P.
Chloroform, $CHCl_3$.....	0·0200	7·65

* *Vide*, " The Propagation of Flame in Gaseous Mixtures," Phil. Mag. ix. p. 260 (Feb. 1930).

Adding an oxygen atom to butane, C_4H_{10}, whose M. I. P. is 3·77, gives

	Slope.	M. I. P.
Ethyl ether, $C_4H_{10}O$	0·445	3·45

Thus, when there is hydrogen present in the molecule the addition of oxygen does not appear to have marked effect; but it is very marked when there are only carbon and oxygen present.

	Slope.	M. I. P.
Carbon dioxide, CO_2	·0091	16·8
Carbon monoxide, CO	·060	2·55

It is the oxygen atoms here that determine the ionic wind, and the fewer they are the greater the cooling.

In consideration of the meaning of these experimental results the energy of formation of the molecule may play some part, but does not appear to be sufficient to account for more than a small fraction of the observed differences, about 0·8 volt in the case of methane.

Nitrogen has been found to have a molecular ionizing potential of 11·5, and hydrogen about 40, yet ammonia NH_3, differs greatly from both, its M. I. P. being 4·02. A combination of nitrogen and oxygen, nitrous oxide, has the following value :—

	Slope.	M. I. P.
Nitrous oxide, N_2O	0·0101	15·29
Ammonia, NH_3	0·038	4·02

Thus the addition of an oxygen atom to a nitrogen molecule has scarcely any influence on the resultant molecular ionizing potential, but the addition of hydrogen to a nitrogen atom lowers it considerably.

There is clearly a regular and characteristic change in the relations of oxygen and hydrogen to carbon and nitrogen, as shown by the electric wind, which may be summarized as follows:—In compounds of carbon and hydrogen the degree of molecular ionization is apparently determined solely by the number of carbon atoms in the molecule of gas; the greater the number the more readily the gas is ionized. When hydrogen is present an added oxygen atom does not appear, in the case of ethyl ether, to have measurable influence. In compounds of carbon and oxygen it is the oxygen that determines the action, making it more difficult. In compounds of nitrogen and oxygen

or hydrogen oxygen has little influence, while hydrogen has a marked effect, in the latter case facilitating ionization. The examination of mixtures of gases by means of the electric wind, the technique of which is not difficult, might

TABLE III.

Gas.	Cooling starts at kv.	Slope of curves.	Relative slope.	Atomic ionizing potential.	Apparent molecular ionizing potential.	
					Volts.	
Argon	24	·0133	1·0	11·5	11·5	A
Neon	30	·0080	0·6	21·5	19·2	N
Helium	45	·0057	0·429	25·4	26·8	He
Hydrogen	37·5	·00364	0·27	13·53	42·4	H_2
Oxygen	22·5	·0220	1·65	13·56	6·9	O_2
Nitrogen	19·5	·0133	1·00	14·49	11·5	N_2
Air.....	19·5	·0133	1·00	—	11·5	$4N_2+O_2$
Methane	29·5	·0135	1·015	14·4	11·3	CH_4
Ethane	32·5	·0242	1·82	12·8	6·32	C_2H_6
Propane	30·5	·0306	2·3	—	5·0	C_3H_8
Butane	33·4	·0406	3·05	—	3·77	C_4H_{10}
Pentane	39·0	·0440	3·3	—	3·49	C_5H_{12}
Acetylene	24·7	·0243	1·825	12·3	6·29	C_2H_2
Ethylene	31·2	·0245	1·84	12·2	6·25	C_2H_4
Chloroform	13·0	·0200	1·5	—	7·65	$CHCL_3$
Ethyl ether	25·0	·0445	3·34	—	3·45	$C_4H_{10}O$
Carbon dioxide ..	17·5	·0091	0·685	—	16·8	CO_2
Carbon monoxide .	22·1	·060	4·5	—	2·55	CO
Nitrous oxide	23·1	·0101	0·76	—	15·29	N_2O
Ammonia	20·0	·038	2·85	—	4·02	NH_3
Carbon disulphide .	32·5	·0133	1·0	—	11·5	CS_2
Water vapour ..	17·5	·02	1·5	—	7·65	OH_2

throw further light on the mechanism of ionization of complex molecules by collision in a field of force.

The results are collected in Table III. (See L. Rolla and G. Piccardi, Phil. Mag. Feb. 1929, no. 42, p. 296, for a recent list of ionizing potentials; and J. C. Morris, Phys. Rev. xxxiii., pp. 456-458, Sept. 1928.)

The observed figures given in Table III. refer to the apparatus in which the tests were made. They can be reduced to any other form of instrument by comparing in each the slopes of the curves of observation with that of any convenient standard gas.

The first column of figures is given for comparison of the relative voltages at which the cooling of the wire begins. These voltages, and to a less degree those of the second column, depend upon the dimensions of the apparatus. The relative values did not change in the various forms of experimental arrangement used.

XCVII. *The Psychophysical Law.*—III. *The Tactile Sense.* *By* P. A. Macdonald, *M.Sc., Ph.D., Hudson's Bay Fellow, and* D. M. Robertson, *M.A., Department of Physics, University of Manitoba, Winnipeg, Canada* *.

WEBER'S Law states that the magnitude of the differential threshold, that is, the strength of the just perceptible increment of a sensory stimulus, bears a constant ratio to the strength of the stimulus at which the differential threshold is determined. In the first part † of this paper it was shown that the law held exactly for the visual sense ; it was further shown that abrupt changes in the value of the ratio occurred at some intensities of the stimulus, probably corresponding to the similar changes of slope observed in curves obtained by plotting the reciprocal of the critical duration of flicker against the logarithm of the stimulating intensity.

Investigations dealing with the behaviour of the differential threshold in the auditory sense ‡ were described in Part II. of the communication, in which it was shown that, while Weber's law did not hold, there was an exact law relating the increment to the total intensity by the equation

$$\Delta I . \log I = C,$$

or, adopting Weber's form,

$$\frac{1}{\frac{\Delta I}{\log I}} = C',$$

* Communicated by Prof. Frank Allen.

† "The Psychophysical Law.—I.", Phil. Mag. ix. p. 817 (1930).

‡ "The Psychophysical Law.—II.," *ibid.* p. 827.

where ΔI is the differential threshold, I the intensity of the stimulus at which ΔI is determined, and C and C′ are constants.

The present paper deals with an extension to the tactile sense of the experimental procedure followed in the investigations in vision and audition, and it will be shown that an accurate law exists in the form

$$\Delta I \,.\log I = C$$

which, as we have stated, seems to hold for the auditory sense.

In examining the tactile sense, the two fundamental principles employed in vision and audition were followed. First, an adequate stimulus was allowed to act on the receptors for a brief period ; its intensity was then suddenly increased by a small amount, thus adding an increment of the stimulus to the same receptors. Second, care was taken to maintain the receptors at their normal sensitivity while successive readings were being made.

Experimental Procedure.

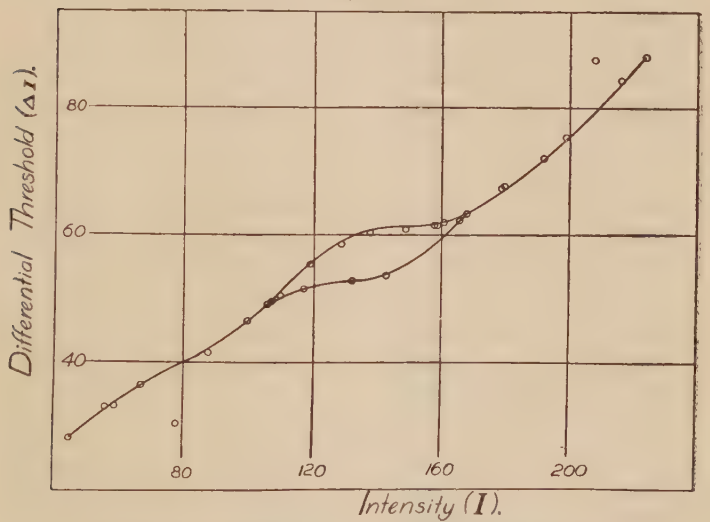
A jet of air was used as the adequate stimulus. The air collected over water in a constant-pressure tank was delivered by a suitable nozzle to the surface of the lower lip, which was kept in position by a chin-rest and a perforated metallic plate. The air-pressure, determined by a water-manometer connected in the air-circuit immediately behind the nozzle, was taken as the strength of the stimulus. Since an increase in pressure was directly proportional to the magnitude of the weight placed on the top of the tank, both the intensity and increment were controlled in this manner.

Air at a definite pressure was allowed to flow through the nozzle directly upon the lip, previously coated with a thin film of vaseline to prevent drying, for a period of approximately one second, after which, while the air was still playing on the lip, the observer suddenly, by a lever, added a small weight to the top of the tank and noted the presence or absence of an increase in sensation. The value of the small weight was taken as a direct measure of the magnitude of the increment, as the actual change in the numerical value of the pressure in this case was too small to be measured by the manometer.

In order that the receptors might return to their normal state of sensitivity, a rest-period of ten minutes was then allowed, following which another trial was made with a decrease or increase in the magnitude of the small weight, depending on whether or not the previous increment had been perceptible. Considerable experience is required to determine in this manner the differential threshold with a high degree of accuracy.

The data obtained for a number of pressures are shown graphically in fig. 1 and given numerically in Table I., where I and ΔI are both expressed in millimetres of air-

Fig. 1.



Showing the behaviour of the differential threshold at different intensities of stimulation.

pressure, the measurements of the former being observed and of the latter computed from the values of the small weights. In fig. 2 the same data are plotted, $\frac{1}{\Delta I}$ against log I, the resulting linear relation showing that the differential threshold is related to the intensity of the stimulus by the equation,

$$\frac{1}{\Delta I} = K \log I + C,$$

and that at certain magnitudes of the intensity the constants suddenly change in value, which is indicated by

TABLE I.—Data for figs. 1 and 2.

Intensity.	Log I.	ΔI.	$\frac{1}{\Delta I} \times 1000$.
45 mm.	1·653	28·0	35·71
56	1·748	33·0	30·30
59	1·771	33·0	30·30
67	1·826	36·1	27·70
78	1·893	30·3	33·00
88	1·945	41·5	24·10
100	2·000	46·5	21·50
108	2·033	49·6	20·16
109	2·037	50·0	20·00
110	2·041	50·5	19·80
117	2·068	51·4	19·46
119	2·076	55·4	18·05
129	2·110	58·6	17·06
132	2·121	52·7	18·98
138	2·140	60·4	16·56
143	2·155	53·6	18·66
149	2·173	60·8	16·45
158	2·199	61·4	16·29
159	2·201	61·4	16·29
161	2·207	61·8	16·18
166	2·220	62·2	16·08
168	2·225	63·5	15·75
179	2·253	67·2	14·88
180	2·255	67·6	14·79
192	2·283	72·1	13·87
199	2·299	75·3	13·28
208	2·318	87·5	11·43
214	2·330	84·3	11·96
224	2·350	88·0	11·36

Intensity and differential threshold are both expressed in mm. of water pressure.

Diameter of air nozzle 0·7 mm.

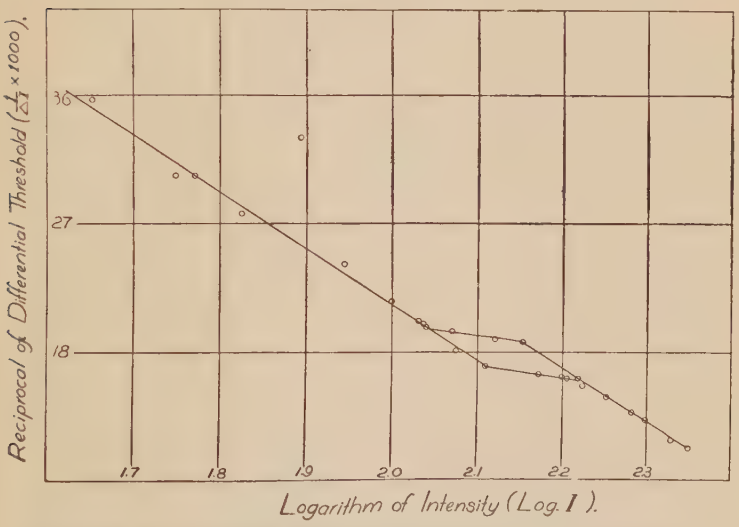
abrupt changes in the slope of the graph. The loop in the curve was obtained by taking readings on different days,

and indicates that the intensity at which changes of slope occur is not constant, but may vary from day to day, a phenomenon which we have observed in vision in both the Weber and Ferry-Porter graphs.

Similarities between Flicker and Increment Phenomena.

Allen and Hollenberg *, by alternating equal periods of stimulation and rest in rapid succession, have succeeded in obtaining a flickering tactile sensation similar in nature to the flickering visual sensation obtained with the flicker photometer.

Fig. 2.



Showing the logarithmic relation existing between the differential threshold and the stimulating intensity.

On plotting the logarithm of the intensity of the stimulus against the critical duration of the stimulus, measured at the point where the sensation has become just continuous, they obtained a linear relation, reproduced here as fig. 3, showing the equation to be

$$D = K \log I + C,$$

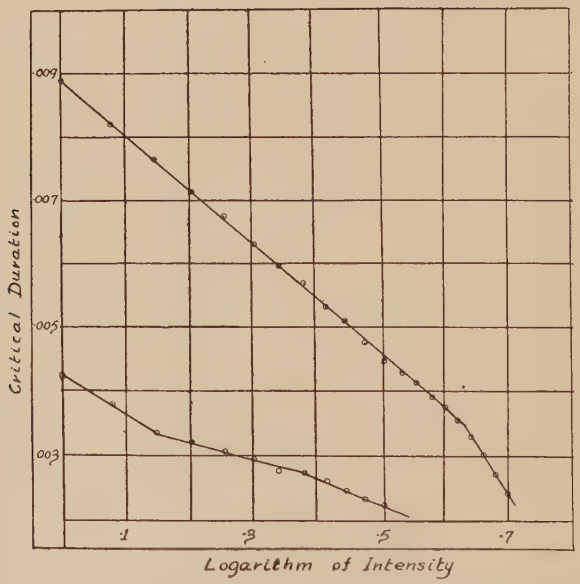
where D is the critical duration of the stimulus and I its intensity.

* Quart. Journ. Exper. Physiol. xiv. No. 4, p. 351 (1924).

The similarity between this curve and that of fig. 2, together with the fact that both the critical duration and the differential threshold are probably closely related to sensation, led us to determine the two curves with the same apparatus over the same range of intensity.

In order to obtain the critical duration curve, the air playing on the lip was interrupted by a cardboard disk containing equal numbers of open and closed equiangular segments, the disk being rotated between the air-nozzle and

Fig. 3.



Critical duration of percussion curve obtained by Allen and Hollenberg.

the protecting plate by a low-velocity synchronous motor. The air-pressure was altered by a needle-valve until the sensations resulting from the individual pulses of air were fused into a just continuous sensation. The duration of a pulse was then computed from the velocity of the motor and the number of segments cut from the disk. Different values of the duration were obtained by substituting disks containing different numbers of segments, the corresponding pressure necessary to produce a continuous sensation being measured in each case. A ten-minute rest period

was observed between successive readings, as in determining the threshold curve. Considerable difficulty was experienced at first in obtaining consistent readings, and after some trials it was concluded that the air-nozzle was too small. A new nozzle of larger bore was substituted, whereupon accurate readings were obtained without difficulty. The resulting data are given in Table II. and shown graphically in fig. 4. It will be seen that two curves are obtained, similar to those found by Allen and Hollenberg, indicating the presence of two groups of tactile receptors.

The change in the size of the nozzle necessitated repetition of the differential threshold curve. Difficulty was

TABLE II.—Data for fig. 4.

	Upper graph.		Lower graph.	
Duration.	I.	Log I.	I.	Log I.
0·0222 sec.	140 mm.	2·146	108 mm.	2·033
0·0166	149	2·173	120	2·079
0·0133	156	2·193	—	—
0·0111	158	2·199	136	2·134
0·0095	171	2·233	143	2·155
0·0075	203	2·308	167	2·223
0·0060	221	2·344	186	2·270
0·0053	245	2·389	200	2·301
0·0044	260	2·415	219	2·340
0·0039	313	2·496	250	2·398
0·0035	354	2·549	297	2·473

Duration given in seconds.
Intensity given in mm. of water-pressure.

here experienced in making accurate increment readings because the nozzle was too large. Readings were obtained finally, however, with sufficient accuracy to enable the intensities at which the changes of slope occur to be located. A comparison of these intensities with those of the critical duration curves reveals close agreement, emphasizing a similarity in the two phenomena.

The intensities at which changes of slope occur in the differential threshold curve are

$$I = 166 \text{ mm.}, \quad I = 246 \text{ mm.},$$

and the corresponding values in the critical duration curve are

$$I = 160 \text{ mm.}, \quad I = 258 \text{ mm.}$$

Fig. 4.

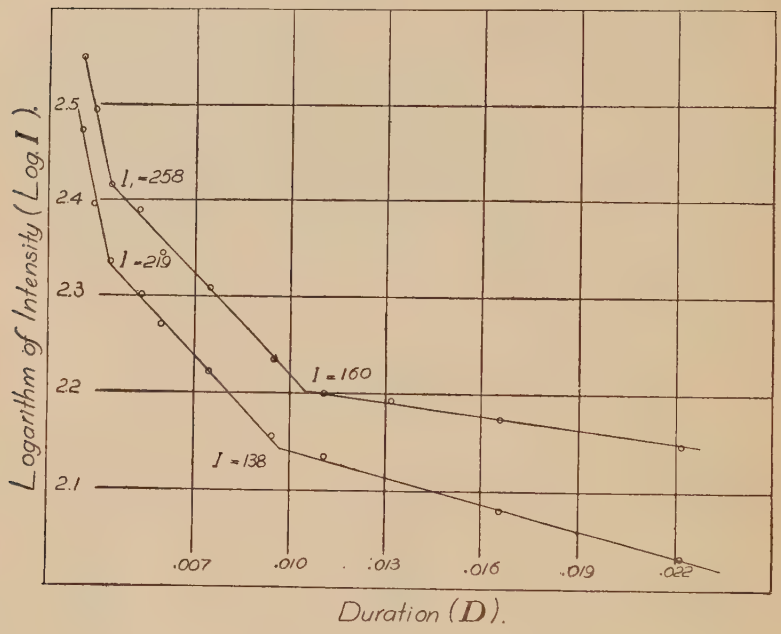
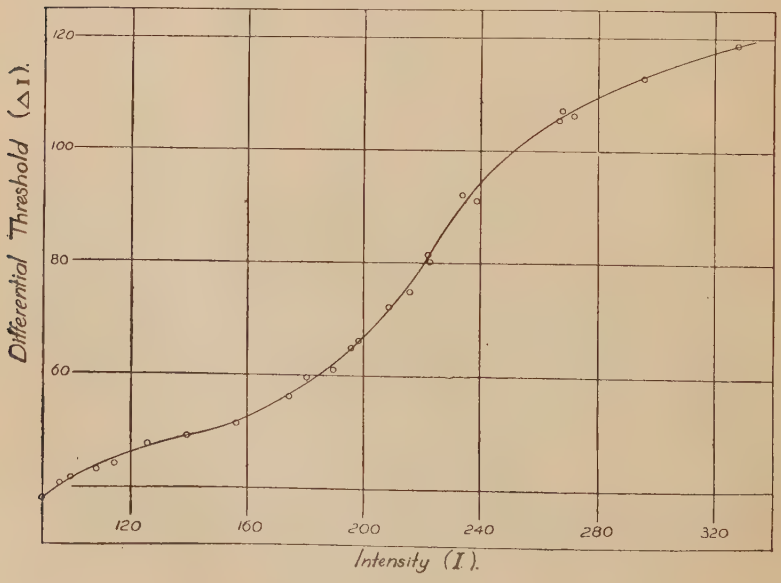

Logarithm of Intensity (Log I).
2.5
2.4
2.3
2.2
2.1
I = 258
I = 219
I = 160
I = 138
.007
.010
.013
.016
.019
.022
Duration (D).

Fig. 5.


Differential Threshold (ΔI).
120
100
80
60
120
160
200
240
280
320
Intensity (I).

The complete curves are given graphically in figs. 5 and 6, and the corresponding numerical data in Table III.

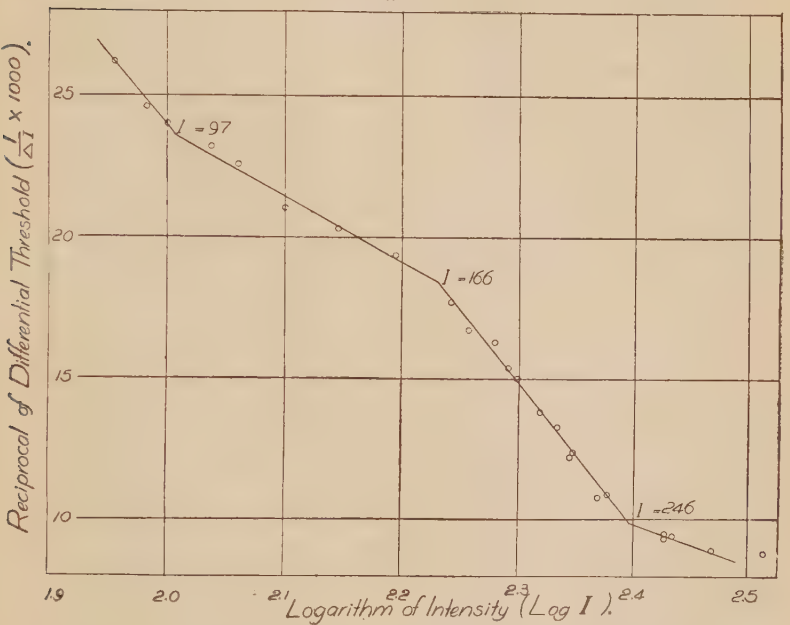
From the work presented in this communication the authors draw three conclusions :—

(1) Weber's law does not hold for the tactile sense.

(2) A definite and accurately determinable relation exists between the differential threshold and the stimulating intensity expressed by the equation

$$\Delta I \,.\, \log I = C.$$

Fig. 6.



(3) There is some intimate relation, at present unknown, between the phenomenon of the critical duration of percussion and that of the least perceptible increment or differential threshold.

Recapitulation.

In the three senses studied, the authors feel confident in stating that the equations,

$$\frac{\Delta I}{I} = C, \text{ in vision,}$$

and

$$\frac{1}{\Delta 1} = \text{K log I, in touch,}$$

TABLE III.—Data for figs. 5 and 6.

Intensity.	Log I.	Δ I.	$\frac{1}{\Delta I} \times 1000$.
79 mm.	1·898	33·60 mm.	29·7
90	1·954	38·10	26·2
96	1·982	40·60	24·6
100	2·000	41·60	24·0
109	2·037	43·10	23·2
115	2·061	44·10	22·6
126	2·100	47·60	21·0
140	2·146	49·10	20·3
157	2·196	51·41	19·4
175	2·243	56·41	17·7
181	2·258	59·60	16·7
190	2·279	61·10	16·3
196	2·292	64·91	15·4
199	2·299	66·60	15·0
209	2·320	72·10	13·8
216	2·334	74·91	13·3
222	2·346	81·60	12·2
223	2·348	80·10	12·4
234	2·369	92·10	10·8
239	2·378	91·10	10·9
267	2·427	105·41	9·5
268	2·428	107·10	9·3
272	2·435	106·10	9·4
296	2·471	112·91	8·9
328	2·516	113·91	8·8

Intensity and differential threshold are both expressed in mm. of water-pressure.

Diameter of nozzle 1·5 mm.

starting from the threshold value, hold exactly over wide ranges of intensity, with suitable changes in constants, and that in the auditory sense the equation

$$\frac{1}{\Delta I} = \text{K log I,}$$

holds exactly for the limited range of intensity obtainable from tonvariators, when employed as the sound-source.

Recent work by other observers in sound has been examined, but it was not possible to test with it the auditory equation, as complete numerical data have not been given.

Moreover, the linear relation with characteristic change of slope would probably be concealed by the practice of taking means not only of individual observer's results, but of the results of a number of different observers. This practice can hardly be considered legitimate for two reasons: first, changes in the state of adaptation of the individual alter the position of the change of slope; and second, means of a group of observers will merge together the individual sharp changes of slope into a curve, since these changes hardly ever occur at the same intensity for different individuals.

Weber's law has also been investigated in the gustatory sense, but owing to the physiological elements involved in such an investigation the results will be published elsewhere, probably in the 'Quarterly Journal of Experimental Physiology.'

XCVIII. *X-Ray Study of Grain Size in Steels of different Hardness Values.* *By* W. A. Wood, *M.Sc., Physics Department, National Physical Laboratory, Teddington, Middlesex* *.

Introduction.

THE particles which compose a solid may be either single crystals of more or less irregular shape or minute aggregates of single crystals. It is with the size of the ultimate single crystals that X-ray investigations are concerned. These may be so large, about 10^{-3} cm. or greater, that the interference lines produced by a given volume illumined by an X-ray pencil are broken up into spots. Each spot is due to one crystal, and from the number of spots it is possible, under correct conditions, to deduce the number of crystals per unit volume and hence an average grain size. On the other hand, they may be so

* Communicated by G. W. C. Kaye, O.B.E., M.A., D.Sc.

small that the interference lines are continuous. In this case, if they are small enough, about 10^{-5} cm. or less, then the diminution in the number of diffracting planes in any one grain will affect the resolving power of the crystal. A measurable broadening of the interference lines may then occur. In the present work measurement of the broadening effect is made for a set of ten samples of stainless steel. The samples had the same chemical composition but differed widely in degree of hardness. The average grain size, which is of a sub-microscopic order of magnitude, is estimated. An account is also given of a relation found to hold between the measured grain size and the hardness of the steels.

A mathematical investigation of the connexion between grain size and the breadth of X-ray interference lines was first put forward by Scherrer * and extended by Laue †. The latter gives a number n which is a measure of the relative breadth of an interference line so far as this breadth depends only on the size of the particles. It is

$$n_{(h_1h_2h_3)} = \frac{\lambda}{4\pi}\sqrt{\Sigma\left(\frac{b\,\mathrm{G}}{m_i}\right)^2}, \quad \mathrm{G} = \frac{\Sigma h_i b_i}{\left|\Sigma h_i b_i\right|}, \quad . \quad (1)$$

where the numbers h_i are integral and the quantities b_i are the usual reciprocal lattice vectors given by the relation

$$b_i = \frac{[a_k a_l]}{(a_i a_k a_l)},$$

in which a_i, a_k, a_l are the vectors defining the primitive translation triplet of a general crystal lattice. The number m_i measures the extent of the particles in the direction a_i.

In the case of a cubic lattice of side a, which holds for the steels investigated, equation (1) simplifies to

$$n = \frac{\lambda}{4\pi}\sqrt{\frac{1}{a^2}\cdot\frac{\Sigma\left(\frac{h_i}{m_i}\right)^2}{\Sigma(h_i)^2}} = \frac{\lambda}{4\pi ma}. \quad . \quad . \quad (2)$$

Thus we have a simple expression which, if n can be obtained in terms of a measurable quantity, will yield the estimated grain size ma.

The value of n was evaluated by Laue for the practical experimental case of a rod of powder of radius r placed at the centre of a circular camera, radius R. It is given in

* P. Scherrer, *Göttingen Nachr.* xcviii. (1918).
† V. Laue, *Zeit. für Kryst.* lxiv. p. 115 (1926).

terms of the half-breadth B of the interference line for which the angle of reflexion is θ. Thus

$$B = \frac{\frac{\pi\omega}{n_h}\left(\frac{r}{R}\right)^2 \cos^3\theta}{\sqrt{1+\left(\frac{\omega r \cos^2\theta}{n_h R}\right)^2 - 1}}, \quad \omega = \frac{1}{1{\cdot}8}. \quad . \quad (3)$$

By the half-breadth is meant the ratio of the total intensity of the interference line to the intensity at the maximum. It is usually estimated by measuring the distance between the two points on each side of the peak where the intensity is half the maximum.

From equation (3) we have, by transposition,

$$n_h = \frac{\omega}{2}\left[\frac{B\cos\theta}{\pi} - \frac{\pi}{B}\left(\frac{r}{R}\right)^2 \cos^3\theta\right]. \quad . \quad . \quad (4)$$

Since we know r, R, θ, and can measure B, we are able from equations (2) and (4) to determine the grain size of the material under consideration.

Two main assumptions are made by Laue. First, the effect of absorption in the powder rod is neglected, and second, all the particles are taken to be of the same size and atomic arrangement. The effect of absorption is important. It means that since points inside the powder rod will reflect X-rays with less intensity than points on the surface, and some points not at all, the effective shape of the rod, as far as the X-rays are concerned, is not the geometric shape. A simple correction, however, has been described by Brill *. It involves a multiplication of the measured half-breadth by a factor $\frac{1}{\sin^2\theta}$. The assumption that the particles are similar has probably less influence on the validity of the result. Patterson †, using a distribution function of the Maxwell type, concludes that the results given by Laue's equations would need correction by 35 per cent. But a symmetrical function of the Gaussian type $s = ce^{-(\mu-\mu_0)^2 p}$ is a preferable assumption, and this leads to average grain size values practically the same as those calculated above (Mark).

Measurement of the Half-breadth.

The interference lines produced by the steels were photometered with the aid of a Moll microphotometer. The

* R. Brill, *Zeit. fur Kryst.* lxviii. p. 387 (1928).
† Patterson. *Cf.* Mark, Far. Trans. (March 1929).

screw and drum motions result in a magnification factor whose value was found to be 6·97, thus facilitating measurements of a high degree of accuracy. For the correct interpretation of the records it is essential to ensure, in the first instance, that the density of a line on the X-ray film is proportional to the intensity of the beam by which it is caused. This has been shown to be the case provided that the density is not too large *. If I_0 is the intensity of the photometer beam incident on a point of a film where the photographic density is D, and I the intensity of the transmitted beam, then D is defined by the relation

$$D = \log_{10} \frac{I_0}{I}.$$

The value of D in the experiments was always less than 2. This was brought about by suitable choice of exposures.

In the second instance, it is necessary to calibrate the microphotometer so that observed galvonometer deflexions can be interpreted in terms of the density of the film for which that deflexion occurs. For this purpose a wedge was utilized. This wedge consisted of seven steps of known relative photographic density. From the microphotometer record could be measured y_0 and y, the galvanometer deflexions corresponding to an incident intensity I_0 and a transmitted intensity I, for each step of the wedge. We have then

$$D = \log \frac{I_0}{I} = F\left(\frac{y_0}{y}\right),$$

and it is necessary to find the most useful way of writing the function F. It is preferable, of course, that the function should be linear. In fig. 1 the known values of D for the wedge are platted against $\log \frac{y_0}{y}$. It appears that from values of $D = 0$ to $D \simeq 0{\cdot}5$, and from values of $D \simeq 0{\cdot}7$ to $D \simeq 1{\cdot}8$ the graph is practically a straight line. The slope of the two portions is different and the intervening part is curved. Therefore, whilst a small density cannot be compared with a heavy one without the use of a separate calibration curve, densities of the same order, if they both lie in one of the above regions, may be compared with the aid of the relation $D = \log \frac{y_0}{y}$. The exposures and development times were such, in the actual experiments, as

* Blunck und Koch, *Ann. Phys.* lxxvii. p. 483 (1925).

to bring the line densities in one linear region. Moreover, all ten steel photographs were simultaneously developed and

Fig. 1.

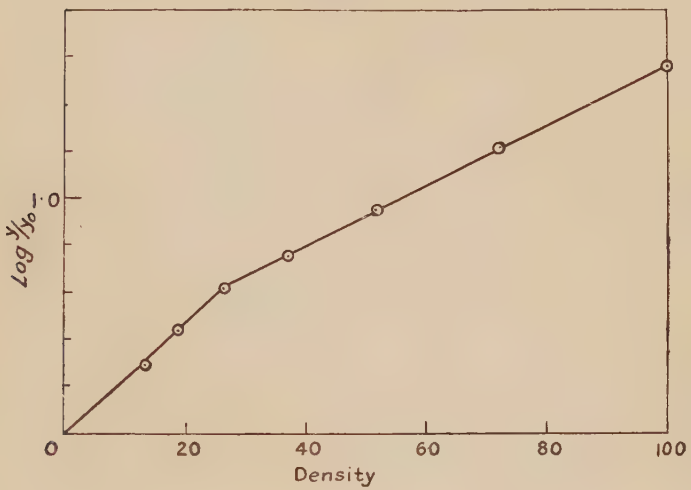
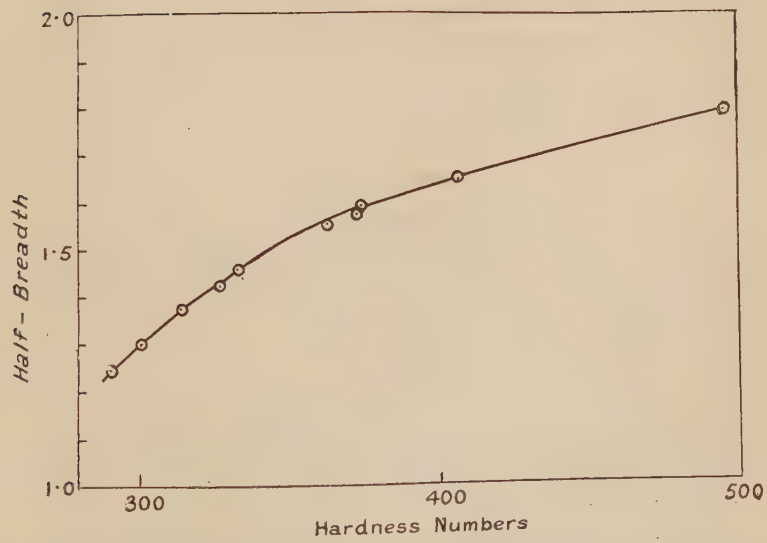


Fig. 2.



fixed for the same periods to avoid differences in photographic contrast.

The Line Breadths and the Hardness Numbers.

The half-breadths were measured on the (200) and (211) lines of the α-iron spectrum produced by the steels. It was found that when the measured breadths were plotted against the hardness numbers a smooth continuous curve resulted. This is illustrated for the (211) by fig. 2. Now the steels were of the same composition, namely, 0·39 per cent. carbon, 0·51 per cent. silicon, 0·028 per cent. sulphur, 0·024 per cent. phosphorus, 0·17 per cent. nickel, 12·45 per cent. of chromium, and of manganese a trace. The variations of hardness were produced by heat treatment which from other data and from the appearance of the accompanying carbide lines does not appear to have greatly affected the nature of the carbides. The grain size might therefore have been expected to be the main factor influencing the hardness, and it is interesting to find that this is suggested by the continuity of the curve. Further, it must be pointed out that the continuity of the relation is independent of any theoretical assumptions about the broadening of the interference lines save the perfectly general and justifiable one that the effect is a function of the size of the diffracting grains. Since, too, it is safe to say that as the line broadens the grain size decreases, the slope of the curve shows that as the hardness increases the grain size decreases at first fairly rapidly and then very slowly. This extends previous results on the subject of grain size and hardness therefore into the region where the grain size is of a sub-microscopic order of magnitude by purely experimental observations.

Grain Size and the Hardness Numbers.

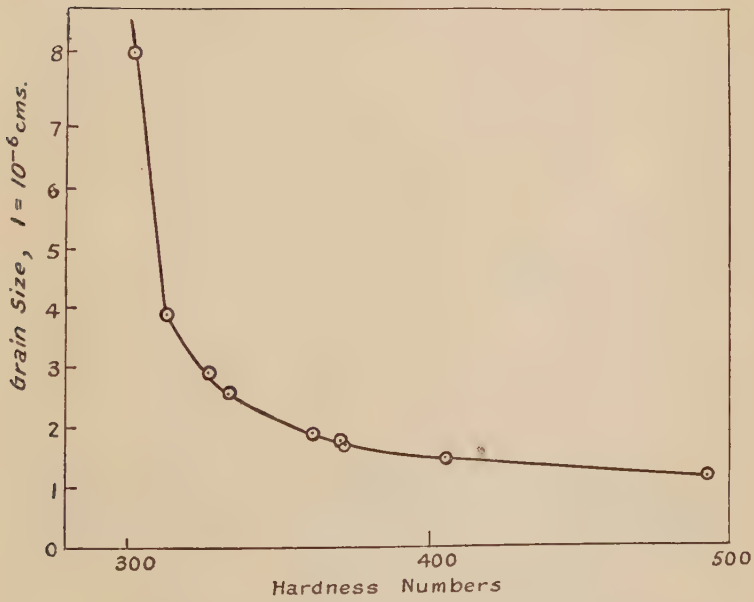
To give a quantitative aspect to the above observation we assume the validity of the equations of Laue and the corrections of Brill. The following were the experimental conditions. The radiation used was FeK_α characteristic ($\lambda = 1{\cdot}932$ Å.) giving the value of θ to be 42° 33′ for the (200) and 55° 54′ for the (211) line. The value of $\left(\frac{r}{R}\right)^2$ was the same for each steel, namely 4×10^{-4}. The exposures were for 1½ hours in a Debye camera using a water-cooled gas tube actuated by a Watson 2 K. V.A. transformer working with a primary current of about 4 amperes at 80 volts. The calculation of the grain size based on either the (200) or (211) line gave practically the same result. Since the correction for absorption is much less in the case of the (211) line the values given by that line are

preferable to a mean of the two values. The (200) values are considered as a check. In Table I., column 1, are given

TABLE I.

Hardness.	Grain size.
290	$28{\cdot}9\times10^{-6}$ cm.
300	8·3 „
313	3·9 „
326	3·0 „
333	2·6 „
361	1·9 „
370	1·8 „
371	1·7 „
404	1·5 „
495	1·1 „

Fig. 3.



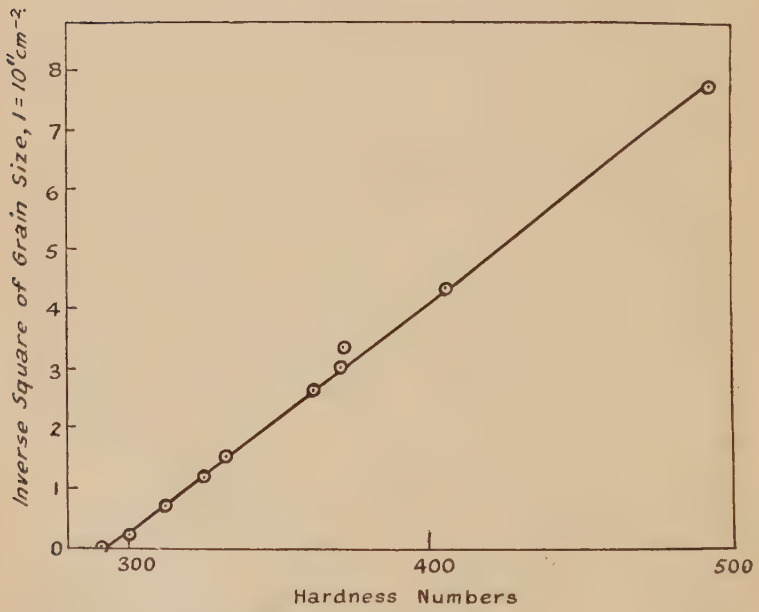
the hardness numbers of the steels, and in column 2 the calculated grain size values. The hardness numbers are expressed in kilogrammes per square millimetre. In fig. 3

the grain size is plotted against the hardness, and it is seen that a similar type of curve to that in fig. 2 is the result.

A physical interpretation of the curve and an indication of its type were next sought. It was found that if the hardness number were plotted against the inverse square of the grain size a definite linear relation appeared. The resulting straight line is depicted in fig. 4. Thus we have that if S is the average grain size in a steel of hardness H, then

$$H = \frac{k}{S^2}, \quad k = \text{constant}.$$

Fig. 4.



Now S is the diameter of the average grain and is of linear dimensions, so that S^2 may be taken as being proportional to the area of surface of the grain. If A is the superficial area of the average grain, then

$$H = \frac{c}{A}, \quad c = \text{constant}.$$

Thus we would appear to have obtained by the application of Laue's equation to the observed broadenings of the interference lines an indication that, other things being equal,

the hardness of this type of steel is a function of the surface area of the grain in a region where the grain size is of the order of 10^{-6} cm. It might be interpreted either as being due to the atomic layers, or possibly carbide material, coating the grain. Alternatively, it may mean that the force required to separate the grains must overcome a type of cohesion force of a definite magnitude per unit surface area and that the purpose of the carbides is mainly to interfere with grain growth. It must be remembered that the hardness numbers are usually determined by measuring the deformation produced by the impression of various loads, so that they are probably a measure of the force necessary to slide one crystal over another. In any case, the application of X-rays in this sphere contributes some data which should be of value to an understanding of the nature and cause of hardness. It is hoped to extend the work to other types of materials and also to cases in which the changes of grain size in steels are accompanied by physical and chemical carbide changes.

The thanks of the writer are due to Dr. G. Shearer for his discussion of the results and to Dr. G. W. C. Kaye, who provided the facilities for the research. The writer is, moreover, very deeply indebted to Mr. V. Stott for kindly loaning the specimens and supplying the hardness numbers determined by him.

Summary.

1. The mathematical investigation of Laue of the effect of particle size on the breadth of X-ray interference lines is applied to the case of samples of steel of different hardness values.

2. The method of measuring the half-breadths of the iron lines by the Moll microphotometer is described. A relation is found to exist between the measured half-breadths and the hardness numbers of the respective steels.

3. From the half-breadths the grain size of the steels is determined with the aid of Laue's equations. The relation between the grain size and the hardness is discussed, the relation being found to agree with the assumption that the hardness varies inversely as the superficial area of the grains.

XCIX. *New Bands in the Secondary Spectrum of Hydrogen.* Part III. *By* D. B. Deodhar, *M.Sc., Ph.D., Physics Department, Lucknow University, Lucknow (India)* *.

AS indicated in the previous paper †, "New Bands, Part II.," a system of a new group of bands is discovered in the violet region of the spectrum, and I wish to deal with that group in the present communication.

The new group in the violet consists of seven bands, and the P(2)-lines of these bands approximately possess the same sequence of frequency differences as exists in the case of the P(2)-lines of the yellow ‡ and the blue bands. The vertical differences of the P, Q, and R branches of these bands are also similar to those in the yellow and the blue regions. This set of bands is weak as compared with the blue, and the set of bands in the blue previously described is weaker than the yellow bands. Like the yellow and the blue, the development of the violet bands also appears to be favoured by the special type of low voltage, low pressure discharge in hydrogen known as the first type discharge according to the nomenclature adopted by Prof. O. W. Richardson. A large mass of strong lines in the visible region first measured by Merton and Barratt §, and later resolved and measured by Gale, Monk, and Lee ‖, have been further resolved and carefully measured recently by Finkelnburg ¶, in whose list many strong lines initially measured as singlets or doublets appear as resolved into many components whose number in certain cases is as large as six. The interpretation of the microphotograph of the first-type spectrogram of hydrogen made in the light of Finkelnburg's tables of wave-lengths offered a great facility in picking up relevant band-lines discussed in the present paper. Owing to the similarity of these bands to those published before, they are named as D bands, with the suffixes 1, 2, 3, etc., to distinguish one band of the group from the other. Further, the letter D is given two dashes for its index to distinguish the violet group from the

* Communicated by the Author.
† Phil. Mag. ix. pp. 37–49 (1930).
‡ Phil. Mag. vii. pp. 466–479 (1928).
§ Phil. Trans. Roy. Soc. A, ccxxii. pp. 369–400 (1922).
‖ Astro-Phys. Journal, lxvii. pp. 89–113 (1928).
¶ *Zeit. für. Phys.* Band lii. Heft 1 & 2, pp. 27, 114 (1928).

blue group. Each of these bands possesses three branches, P, Q, and R, having a common null line.

The details of these bands are given in Table I. The band-lines are represented by their wave-numbers, the values of which are taken from Finkelnburg's tables. The intensity estimates in Finkelnburg's lists appear to be rather high, but this may be due to the strong current and the high voltage used in running the discharge-tube in his experiments. However, his intensity values are given in brackets which follow the frequencies of lines. These intensity estimates are next followed by the author's intensity estimates from the first-type plate. In certain cases of lines which are not given in Finkelnburg's tables the frequencies are taken from tables of Gale, Monk, and Lee *, Tanaka †, or Deodhar ‡. Such lines are indicated by the letters G., M., L., T., or D. put underneath the corresponding frequencies. The band-lines set forth here have got very few important claims by other series; but in those cases where such a claim exists the fact is indicated by giving the proper reference underneath such a line. The intensities and the first-type characters are followed by the first and second differences. The horizontal and the vertical differences are given in Tables II. and III. respectively.

The intensity of the line 25030·11 which figures as $D''_1P(4)$ is not known definitely, as it is mixed up with 25031·45 M.B., which is broad on the first-type plate and whose intensity is one. 25319·33 $D''_1Q(4)$ is the resolved part of 25321·65 T, which comes up in the first-type spectrum. $D''_3P(2)$ is identical with $D''_2Q(2)$. This double claim appears to be justifiable when we consider the intensity of the line 25551·39. Finkelnburg gives the number 2 for its intensity, and on the whole there are very few strong lines in these bands. 25727·09 figures as $D''_5P(2)$ and also as $D''_2R(1)$. It is the component of 25754·70 M.B.(0). which comes out in the first-type spectrum with much strength. However, its claim as $D''_5P(2)$ seems to be superior to its allocation as $D''_2R(1)$. It may as well be remembered that this line is not claimed anywhere else. 25659·60 $D''_3Q(3)$ does not appear in the author's published list of new lines, but it is present in the unpublished

* Astro-Phys. Journal, lxvii. pp. 89–113 (1928).
† Proc. Roy. Soc. A, cvii. pp. 592–606 (1925).
‡ Proc. Roy. Soc. A, cxiii. pp. 420–432 (1926).

Table I.

$D''_1P(m)$.

m.		Δ_1.	Δ_2.
2.	25250·22(0)(<0)		
		>100·89	
3.	25149·33(00)(?)		>18·33
		>119·22	
4.	25030·11(0)(?)		>10·31
		>129·53	
5.	24900·58(00)(ab)		

$D''_2P(m)$.

m.		Δ_1.	Δ_2.
2.	25401·95(00)(<0)		
		>105·40	
3.	25296·55(0)(<0)		>20·74
		>126·14	
4.	25170·41(00)(<0)		> 5·74
		>131·88	
5.	25038·53(0)(ab)		

$D''_1Q(m)$.

m.		Δ_1.	Δ_2.
1.	25448·74(0)(<0)		
		>29·99	
2.	25418·75(00)(<0)		>11·40
		>41·39	
3.	25377·36(00)(<0)		>16·64
		>58·03	
4.	25319·33(0)(<0)		> 8·38
		>66·41	
5.	25253·92(0)(ab)		

$D''_2Q(m)$.

m.		Δ_1.	Δ_2.
1.	25578·37(0)(<0)		
		>26·98	
2.	25551·39(2)(<0)		>11·12
	$D''_2P(2)$	>38·10	
3.	25513·29(0)(ab)		>13·45
		>51·55	
4.	25461·74(00)(<0)		> 5·39
		>56·94	
5.	25404·80(2)(<0)		

$D''_1R(m)$.

m.		Δ_1.	Δ_2.
1.	25616·60(0)(0)		
		>30·22	
2.	25646·82(0)(0)		>10·83
		>19·39	
3.	25666·21(00)(ab)		>12·44
		> 6·95	
4.	25673·16(0)(ab)		

$D''_2R(m)$.

m.		Δ_1.	Δ_2.
1.	25727·09(00)(<0)		
	D''_5 P (3)	>41·47	
2.	25768·56(1)(1)		> 4·94
		>36·53	
3.	25805·09(0)(<0)		>13·36
		>23·17	
4.	25868·26(0)(<0)		

Table I. (*cont.*).

$D''_3P(m)$.

m.		Δ_1.	Δ_2.
2.	25551·39(2)(<0)		
		>110·83	
3.	25440·56(*r*)(*r*)		>21·01
	D.	>131·84	
4.	25308·72(0)(<0)		> 4·26
		>136·10	
5.	25172·62(0)(<0)		

$D''_4P(m)$.

m.		Δ_1.	Δ_2.
2.	25699·94(00)(<0)		
		>115·23	
3.	25584·71(2)(<0)		>20·74
		>135·97	
4.	25448·74(4)(<0)		> 1·62
		>137·59	
5.	25311·15(00)(*ab*)		

$D''_3Q(m)$.

m.		Δ_1.	Δ_2.
1.	25720·77(0)(*ab*)		
		>25·70	
2.	25695·07(2)(<0)		> 9·77
		>35·47	
3.	25659·60(*r*)(*rd*)		>12·05
		>47·52	
4.	25612·08(0)(*ab*)		> 5·55
		>53·07	
5.	25559·01(0)(*ab*)		

$D''_4Q(m)$.

m.		Δ_1.	Δ_2.
1.	25899·02(<0)(*ab*)		
		>25·18	
2.	25873·84(0)(*ab*)		>10·53
		>35·71	
3.	25838·13(4)(<0)		> 8·97
		>44·68	
4.	25793·45(0)(*ab*)		> 6·19
		>51·87	
5.	25741·58(00)(*ab*)		

$D''_3R(m)$.

m.		Δ_1.	Δ_2.
1.	25864·55(1)(*ab*)		
		>49·83	
2.	25914·38(2)(<0)		> 1·89
		>47·94	
3.	25962·32(0)(*ab*)		>12·50
		>35·44	
4.	25997·76(<0)(*ab*)		

$D''_4R(m)$.

m.		Δ_1.	Δ_2.
1.	26072·76(*r*)(*r*)		
	D.	>55·00	
2.	26127·76(0)(*ab*)		>00·32
		>55·32	
3.	26183·08(1)(<0)		>14·06
		>41·26	
4.	26224·34(0)(0)		

Table I. (*cont.*).

$D''_5P(m)$.

m.		Δ_1.	Δ_2.
2.	25848·05(1)(0)		
		> 120·96	
3.	25727·09(00)(<0)		> 17·25
		> 138·21	
4.	25588·88(0)(*rd*)		> 7·20
		> 145·41	
5.	25443·47(0)(*ab*)		

$D''_5Q(m)$.

m.		Δ_1.	Δ_2.
1.	26114·38(0)(*ab*)		
		> 23·32	
2.	26091·06(0)(<0)		> 5·16
		> 28·48	
3.	26062·58(1)(<<0)		> 11·81
		> 40·29	
4.	26022·29(0)(<0)		> 8·07
		> 48·36	
5.	25973·93(00)(*ab*) G.M.L.		

$D''_5R(m)$.

m.		Δ_1.	Δ_2.
1.	26357·05 (*r*) (*r*) D.		
		> 69·24	
2.	26426·29 (0) (<0)		> 0·20
		> 69·04	
3.	26495·33 (*r*) (*r*)		> 11·81
		> 57·23	
4.	26552·56 (00) (*ab*)		

$D''_6P(m)$.

m.		Δ_1.	Δ_2.
2.	25994·82(1)(0)		
		> 124·31	
3.	25870·51(2)(1)		> 21·60
		> 145·81	
4.	25724·70(3)(1)		> 10·86
		> 156·67	
5.	25568·03(2)(0)		

$D''_6Q(m)$.

m.		Δ_1.	Δ_2.
1.	26368·02(7)(0)		
		> 21·26	
2.	26346·76(4)(0)		> 5·06
		> 26·32	
3.	26320·44(0)(*ab*)		> 14·06
		> 40·38	
4.	26280·06(0)(<0)		> 6·54
		> 46·92	
5.	26233·14(1)(*ab*)		

$D''_6R(m)$.

m.		Δ_1.	Δ_2.
1.	26719·53 (0) (<0)		
		> 77·63	
2.	26797·16 (0) (<0)		> 0·10
		> 77·53	
3.	26874·69 (0) (*ab*) G.M.L.		> 6·54
		> 70·99	
4.	26945·68 (0) (prob. *present*)		

TABLE I. (*cont.*).

$D''_7P(m)$.

m.		Δ_1.	Δ_2.
2.	26136·88(2)(0)		
		> 130·01	
3.	26006·87(1)(0)		> 17·76
		> 147·77	
4.	25859·10(1)(*ab*)		> 9·26
		> 157·03	
5.	25702·07(00)(<0)		

$D''_7Q(m)$.

m.		Δ_1.	Δ_2.
1.	26714·37(1)(*r*)		
		> 20·66	
2.	26693·71(0)(*ab*)		> 4·82
		> 25 48	
3.	26668·23(0)(*ab*)		> 8·19
	F.	> 33 67	
4.	26634·56(*rd*)(*ab*)		> 10·31
	D.	> 43·98	
5.	26590·58(0)(0)		

$D''_7R(m)$.

m.		Δ_1.	Δ_2.
1.	27270·71(5)(1)		
		> 83·68	
2.	27354·39(*r*)(*r*)		> 5·96
	D.	> 89·64	
3.	27444·03(*r*)(*r*)		> 10·30
	D.	> 79·4	
4.	27523·37 (calculated)		

TABLE II.

Horizontal Differences of P(m)'s, Q(m)'s, and R(m)'s.

P(m).

	$D''_2-D''_1$.	$D''_3-D''_2$.	$D''_4-D''_3$.	$D''_5-D''_4$.	$D''_6-D''_5$.	$D''_7-D''_6$.
P(2).....	151·73	149·44	148·55	148·11	146·77	142·06
P(3).....	147·22	144·01	144·15	142·38	143·42	136·36
P(4).....	140·30	138·31	140·02	140·14	135·82	134·40
P(5).....	137·95	134·09	138·53	132·32	134·56	134·04

Q(m).

Q(1).....	130·03	142·40	178·25	215·36	253·64	346·35
Q(2).....	132·64	143·68	178·77	217·22	255·70	346·95
Q(3).....	135·93	146·31	178·53	224·45	257·86	347·79
Q(4).....	142·41	150·34	181·37	228·84	257·37	354·50
Q(5).....	150·88	154·21	182·57	232·35	259·21	357·44

R(m).

R(1).....	110·49	137·46	208·21	284·29	362·48	551·18
R(2).....	121·74	145·82	213·38	298·53	370·87	557·23
R(3).....	138·88	157·23	220·76	312·25	381·00	567·69
R(4).....	155·10	169·50	226·58	328·22	393·12	577·39

TABLE III.

Vertical Differences of P(m), Q(m), and R(m) lines.

P(m)'s.

Band.	P(2)−P(3).	P(3)−P(4).	P(4)−P(5).
D''_1.....	100·89	119·22	129·53
D''_2.....	105·40	126·14	131·88
D''_3.....	110·83	129·41	136·10
D''_4.....	115·23	135·97	137·59
D''_5.....	120·96	138·21	145·41
D''_6.....	124·31	145·81	156·67
D''_7.....	130·01	147·77	157·03

Q(m)'s.

	Q(1)−Q(2).	Q(2)−Q(3).	Q(3)−Q(4).	Q(4)−Q(5).
D''_1.....	29·99	41·39	58·03	65·41
D''_2.....	26·98	38·10	51·55	56·94
D''_3.....	25·70	35·47	47·52	53·07
D''_4.....	25·18	35·71	44·68	51·87
D''_5.....	23·32	28·48	40·29	48·36
D''_6.....	21·26	26·32	40·38	46·92
D''_7.....	20·66	25·48	33·76	43·98

TABLE III. (*cont.*)

R(m)'s.

	R(1)−R(2).	R(3)−R(2).	R(4)−R(3).
D''_1.....	30·22	19·39	6·95
D''_2.....	41·47	36·53	23·17
D''_3.....	49·83	47·94	35·44
D''_4.....	55·00	55·32	41·26
D''_5.....	69·24	69·04	57·23
D''_6.....	77·63	77·53	70·99
D''_7.....	83·68	89·63	79·05

list under the heading of doubtful lines on the first-type plate. The existence of this line is now confirmed by Finkelnburg's observation; 25584·71, figuring as $D''_4P(3)$, is Tanaka's line, and its intensity as given by him is only p, though its intensity is 2 in Finkelnburg's tables. 25448·74 $D''_4P(4)$ is very strong according to Finkelnburg, but according to Tanaka its intensity is only p. On the first-type plate also its intensity is much less than zero. Similarly, 25838·13 is (4) in Finkelnburg's table; but according to Merton and Barratt its intensity is zero. In the first-type spectrum its intensity is less than zero. 26062·58 $D''_5Q(3)$ given by Finkelnburg was originally observed on the first-type plate, but it was not then published, as it was difficult to measure owing to its faintness. In Finkelnburg's table it appears as a strong line. 26280·06 $D''_6Q(4)$ must be mixed up with 26275·27 D, which is wide on the first-type plate. This line seems to be probably resolved from 26275·37 D (*rw*). The calculated wave-number for $D''_6R(3)$ is 26875·80. The corresponding line in G., M., and L.'s tables is given by 26874·69. This line is difficult to measure according to G., M., and L. Finkelnburg also finds it difficut to measure, and omits the fractional part of the wave-length value. This shows that the value of the wave-number in the tables is inaccurate. 25702·07 F. figures as $D''_7P(5)$, and it is resolved from 25704·34 M.B., whose intensity is 3 on the first-type plate. 27270·71 M.B. figures as $D''_7R(1)$; its intensity is 5 according to Finkelnburg, but only 1 according to Merton and Barratt and also according to the first-type spectrum. 27523·37 $D''_7R(4)$ is a calculated wave-number which does not appear in published tables. A very faint line corresponding to the wave-number appears to be present on the

first-type plate. This portion of the spectrum is specially difficult to measure, on account of the diffuse nature of the lines and the superposition of a continuous background. This calculated line is not used in determining the band-constants.

The horizontal and the vertical differences of P's, Q's, and R's of all the bands are arranged in Tables II. and III. The fairly systematic run of the successive horizontal differences is evident from Table II. Table III. shows the systematic nature of variation of the vertical differences of P, Q, and R lines. The vertical differences of the band-lines in the present paper are very much like those in the yellow and the blue. The P(2)—P(3) differences of the yellow, the blue, and the violet bands gradually rise from 99, 98, and 100 for the first bands, and go up to 130, 132, and 130 respectively for the last bands. The Q(1)—Q(2) differences begin from 29, 30, and 30, and gradually go down to 21 for the last band in the yellow, the blue, and the violet alike. The R(2)—R(1) values for the yellow and blue start from 26 and 29 respectively for the first band, and they gradually ascend up to 82 and 83 for the seventh band. Also in the case of violet bands the R(2)—R(1) values gradually go up from 30 for the first band to 83 for the seventh band. All these differences clearly indicate the similarity of the bands in the yellow, the blue, and the violet.

All these bands consist of single P, Q, and R branches, amongst which the combination principle such as $Q(m+1)+Q(m)=P(m+1)+R(m)$ is strictly obeyed. The initial and the final term-differences are tabulated in Tables IV. and V. From these term-differences one can easily evaluate the moments of inertia of the emitters of the bands. The values of the initial and the final term-differences can also serve as a check upon the correct agreement of the combination principle. The frequencies of the null lines, the moments of inertia, the correction terms due to the electronic angular moments, and other band constants are assembled in Table VI. The properties of lines and the systematic variation of the successive differences from the first band to the seventh band show that these bands are related. One observes the same systematic variations in the values of the null lines, which go on gradually increasing from one band to the other. The initial moment of inertia in each case is larger

Table IV.

Initial Terms.

Band.	m.	R(m) −Q(m).	Q(m—1) −P(m—1).	Means.	Term diff.	2nd diff.
D''_1	1 ...	167·86	166·53	168·18	F(2)—F(1)	
						> 59·87
	2 ...	228·07	228·03	228·05	F(3)—F(2)	
						> 60·98
	3 ...	288·85	289·22	289·03	F(4)—F(3)	
						> 64·55
	4 ...	353·83	353·34	353·58	F(5)—F(4)	
D''_2	1 ...	148·72	149·44	149·08	F(2)—F(1)	
						> 67·87
	2 ...	217·17	216·74	216·95	F(3)—F(2)	
						> 74·61
	3 ...	291·80	291·33	291·56	F(4)—F(3)	
						> 74·83
	4 ...	366·52	366·27	366·39	F(5)—F(4)	
D''_3	1 ...	143·78	143·68	143·74	F(2)—F(1)	
						> 75·43
	2 ...	219·31	219·04	219·17	F(3)—F(2)	
						> 83·87
	3 ...	302·72	303·36	303·04	F(4)—F(3)	
						> 82·99
	4 ...	385·68	386·39	386·03	F(5)—F(4)	
D''_4	1 ...	173·74	173·90	173·82	F(2)—F(1)	
						> 79·85
	2 ...	253·92	253·42	253·67	F(3)—F(2)	
						> 91·16
	3 ...	344·95	344·71	344·83	F(4)—F(3)	
						> 85·83
	4 ...	430·89	430·43	430·66	F(5)—F(4)	
D''_5	1 ...	242·67	243·01	242·84	F(2)—F(1)	
						> 92·52
	2 ...	335·23	335·49	335·36	F(3)—F(2)	
						> 97·72
	3 ...	432·75	433·41	433·08	F(4)—F(3)	
						> 97·23
	4 ...	530·27	530·46	530·31	F(5)—F(4)	
D''_6	1 ...	351·51	351·94	351·72	F(2)—F(1)	
						> 98·45
	2 ...	450·40	449·93	450·17	F(3)—F(2)	
						> 105·43
	3 ...	555·84	555·36	555·60	F(4)—F(3)	
						> 109·76
	4 ...	665·62	665·11	665·36	F(5)—F(4)	
D''_7	1 ...	556·34	556·83	556·58	F(2)—F(1)	
						> 104·44
	2 ...	660·68	661·36	661·02	F(3)—F(2)	
						> 114·60
	3 ...	775·79	775·46	775·62	F(4)—F(3)	
						> 112·89
	4 ...	888·51	888·51	888·51	F(5)—F(4)	

TABLE V.

Final Terms.

Band.	m.	R(m) −Q(m+1).	Q(m) −P(m+1).	Means.	Term diff.	2nd diff.
D''_1	1 ...	197·85	198·52	198·18	$f(2)-f(1)$	
						> 71·26
	2 ...	269·46	269·42	269·44	$f(3)-f(2)$	
						> 77·62
	3 ...	346·88	347·25	347·06	$f(4)-f(3)$	
						> 71·05
	4 ...	419·24	418·75	418·99	$f(5)-f(4)$	
D''_2	1 ...	175·70	176·42	176·06	$f(2)-f(1)$	
						> 78·99
	2 ...	255·27	254·84	255·05	$f(3)-f(2)$	
						> 88·06
	3 ...	343·35	342·68	343·11	$f(4)-f(3)$	
						> 80·22
	4 ...	423·46	423·21	423·33	$f(5)-f(4)$	
D''_3	1 ...	169·48	169·38	169·43	$f(2)-f(1)$	
						> 96·22
	2 ...	254·78	254·51	254·64	$f(3)-f(2)$	
						> 95·92
	3 ...	350·24	350·88	350·56	$f(4)-f(3)$	
						> 88·54
	4 ...	438·75	439·46	439·10	$f(5)-f(4)$	
D''_4	1 ...	198·92	199·08	199·00	$f(2)-f(1)$	
						> 90·38
	2 ...	289·63	289·15	289·38	$f(3)-f(2)$	
						> 100·13
	3 ...	389·63	389·39	389·51	$f(4)-f(3)$	
						> 93·02
	4 ...	482·76	482·30	482·53	$f(5)-f(4)$	
D''_5	1 ...	265·99	266·33	266·16	$f(2)-f(1)$	
						> 97·68
	2 ...	363·71	363·97	363·84	$f(3)-f(2)$	
						> 109·49
	3 ...	473·04	473·70	473·37	$f(4)-f(3)$	
						> 105·35
	4 ...	578·63	578·82	578·72	$f(5)-f(4)$	
D''_6	1 ...	372·77	373·20	372·95	$f(2)-f(1)$	
						> 103·53
	2 ...	476·72	476·25	476·48	$f(3)-f(2)$	
						> 119·52
	3 ...	596·27	595·74	596·00	$f(4)-f(3)$	
						> 115·28
	4 ...	712·54	712·03	712·28	$f(5)-f(4)$	
D''_7	1 ...	577·00	577·49	577·24	$f(2)-f(1)$	
						> 109·26
	2 ...	686·16	686·84	686·50	$f(3)-f(2)$	
						> 122·79
	3 ...	809·46	809·13	809·29	$f(4)-f(3)$	
						> 123·20
	4 ...	932·79	932·49	932·49	$f(5)-f(4)$	

TABLE VI.—Band Constants.

Band.	ν_0. From Q(1).	ν_0. From P(2).	ν_0. From R(1).	F(2).	F(1).	f(2).	f(1).	P.	ρ.	Initial Moment of Inertia.	Final Moment of Inertia.
D''_1...	25473·90	25473·83	25473·84	327·91	159·71	383·32	185·22	—1·31	—1·38	$9{\cdot}39\times10^{-41}$ gm. cm.^{2}	$7{\cdot}76\times10^{-41}$ gm. cm.^{2}
D''_2 ..	25599·76	25599·36	25599·65	245·52	96·91	294·32	118·19	—0·69	—0·73	8·15 ,, ,,	7·00 ,, ,,
D''_3...	25740·05	25740·52	25740·36	219·08	74·99	264·12	94·58	—0·41	—0·49	9·04 ,, ,,	6·49 ,, ,,
D''_4...	25918·99	25919·75	25919·30	286·72	112·67	332·48	132·95	—0·68	—0·72	6·93 ,, ,,	6·15 ,, ,,
D''_5...	26147·47	26146·53	26147·20	450·31	207·91	506·39	240·73	—1·22	—1·22	5·98 ,, ,,	5·66 ,, ,,
D''_6...	26399·87	26399·91	26400·51	816·98	464·83	869·92	497·32	—2·07	—2·10	5·61 ,, ,,	5·34 ,, ,,
D''_7...	26744·12	26743·74	26744·44	1774·90	1218·24	1825·10	1248·31	—3·83	—3·78	5·30 ,, ,,	5·06 ,, ,,

than the final moment of inertia, and the values of these moments of inertia gradually go on descending from a high value for the first band to a low value for the seventh band.

Remembering that R(m) line is due to a quantum jump $m+1 \rightarrow m$, P (m) line due to a $m-1 \rightarrow m$ jump, and the Q(m) line results when the quantum number stays unchanged, one can represent them in the usual equation form as :—

$$\left.\begin{aligned} \mathrm{R}(m) &= \nu_0 + \mathrm{F}(m+1) - f(m), \\ \mathrm{Q}(m) &= \nu_0 + \mathrm{F}(m) - f(m), \\ \mathrm{P}(m) &= \nu_0 + \mathrm{F}(m-1) - f(m). \end{aligned}\right\} \text{(A)}$$

Here ν_0 stands for the frequency of the null line and F and f represent the initial and the final state of the molecules. From these equations we can get expressions for term-differences. For instance, we have from (A) above,

$$\left.\begin{aligned} &\mathrm{F}(m+1) - \mathrm{F}(m) = \mathrm{R}(m) - \mathrm{Q}(m) = \mathrm{Q}(m+1) - \mathrm{P}(m+1) \\ &\qquad \text{initial term-differences, and} \\ &f(m+1) - f(m) = \mathrm{R}(m) - \mathrm{Q}(m+1) = \mathrm{Q}(m) - \mathrm{P}(m+1) \\ &\qquad \text{final term-differences.} \end{aligned}\right\} \text{(B)}$$

By giving suitable integral values to the quantum number m in (B), and substituting the values of relevant frequencies of lines, one can obtain successive differences, which are worked out and tabulated in Tables IV. and V. It is seen from (B) that these term-differences can be got in two ways. The means of such two values are tabulated in the fourth column of Tables IV. and V., and the successive differences of these means are placed in the sixth column of these tables. These differences, which are called second differences, are inversely proportional to the moments of inertia. The final and the initial second differences are known to be $2b$ and 2B respectively ; and it is also known that $\mathrm{I}' = h/8\pi^2 c\mathrm{B}$ and $\mathrm{I}'' = h/8\pi^2 cb$, where I′ is the initial moment of inertia and I″ is the final moment of inertia of the molecule about the axis perpendicular to the line joining the nuclei, h is Planck's constant, and c the velocity of light.

In general the initial and the final terms may be represented by the following equations :—

$$\left.\begin{aligned} \mathrm{F}(m) &= \mathrm{B}(m-p)^2, \\ f(m) &= b(m-\rho)^2, \end{aligned}\right\} \text{(C)}$$

where P and ρ are Kratzer's correction terms. These correction terms can be evaluated by using the means in Tables IV. and V., and the second differences of the means. The null lines can hence be quickly calculated from any one of the three equations in (A). The frequencies of the null lines have been calculated by using Q(1), P(2), and R(1) lines for each band, and the three values so obtained agree quite well with one another.

The values of moments of inertia for these bands are of the same order as those for the yellow and the blue band, and this fact, along with the other similarities, indicates that the emitter of these bands is an excited hydrogen molecule (H_2). In deriving the values of moments of inertia use is made of only one of the three values of B or b for each band, but, by taking their average values into consideration, it appears that the final moment of inertia for the D_1 bands in the yellow, the blue, and the violet possesses the same value, while the initial moments of inertia for D_1 bands of yellow, blue, and violet colours are different from one another. The same is the case with D'_2's. D'_3's, and the others. This fact appears to suggest that the final excitation condition of the molecule is the same for all the three D_1 bands, while their initial excitation conditions are different from one another. However, this question of interconnexion of these bands will be taken up later on, after the matter is thoroughly investigated.

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C. *On Mutual Transference of Torsional and Pendulous Oscillations.* *By* G. Subrahmaniam *.

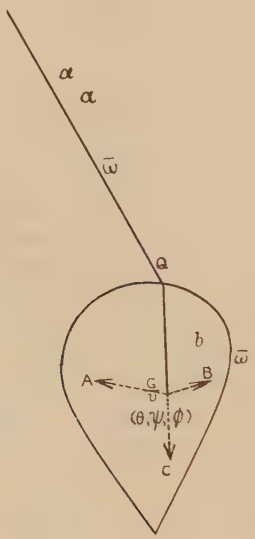
A FEW years ago, in connexion with my extensive study of the dependence of logarithmic decrement on the amplitude of torsional oscillations leading to the determination of the coefficients of viscosity of some metals (Phil. Mag. April 1925, October 1925, May 1926, and April 1927 ; also Landolt & Börnstein's tables), I had an occasion to observe closely the torsional oscillations of quite

* Communicated by the Author.

a large number of wires, of lengths and of thicknesses varying over a wide range of values. In certain cases it was noticed (*l. c.* April 1925, p. 714) that there was a mutual transference of activity from torsional to pendulous states.

It is evident that such a transference is possible when the centre of gravity of the solid of revolution does not lie along the axis, or when the point of attachment of the wire to the solid is different from the extremity of an axis of the solid. The following solution of this problem affords an interesting application of the principle of moving axes and Eulerian coordinates.

Fig. 1.



Let a solid of revolution be suspended by a wire, the point of attachment Q being different from the extremity of an axis of the solid; let $\bar{u}$ be the velocity of the free extremity of the wire, $\bar{v}$ that of the c.g. of the body relative to the lower extremity of the wire, and $\bar{w}$ the velocity of a particle m relative to the c.g. of the body.

The kinetic energy T of the body of total mass M

$$= \Sigma \tfrac{1}{2} m(\bar{u}+\bar{v}+\bar{w})^2$$

$$= \tfrac{1}{2}\{m(\bar{u}^2+\bar{v}^2+\bar{w}^2) + 2\Sigma m(\bar{u}\bar{v}) + 2\Sigma m(\bar{v}\bar{w}) + 2\Sigma m(\bar{u}\bar{w})\}$$

$$= \tfrac{1}{2}\mathrm{M}(\bar{u}^2+\bar{v}^2) + \tfrac{1}{2}\Sigma m\bar{w}^2 + \mathrm{M}\bar{u}\bar{v} + \bar{v}(\Sigma m\bar{w}) + \bar{u}(\Sigma m\bar{w})$$

$$= \tfrac{1}{2}\mathrm{M}(\bar{u}^2+\bar{v}^2) + \tfrac{1}{2}\Sigma m\bar{w}^2 + \mathrm{M}\bar{u}\bar{v}.$$

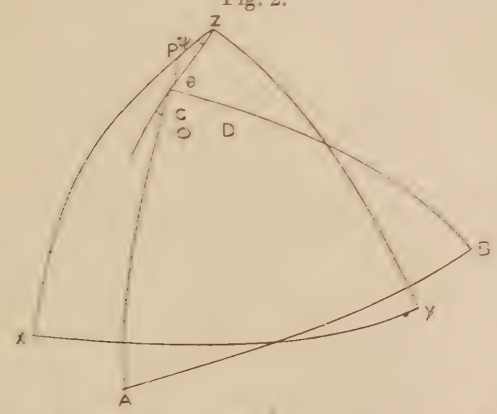
Let G be the c.g. of the solid, $GQ=h$ and "a" be the length of the wire. Take axis GC in the direction of the wire produced, GB perpendicular to GC lying in the plane containing wire and axes of the solid of revolution. Let GA be perpendicular to GB and GC.

Let the Eulerian angles of QG be θ, ψ, ϕ, with respect to Gx, Gy, Gz, the positions of GA, GB, GC when the body is in equilibrium. Let GD be drawn in the direction of wire produced, and α be the inclination of GD to vertical.

Now to find the twist of the wire. For small displacements the amount of twist depends on initial and final positions only, and is independent of path. Produce arc AC to meet zx in P. Then PCz may be considered to be a plane Δ,

$$\angle cPx = \angle Pcz + \angle Pzc = \phi + \psi.$$

Fig. 2.



The twist of wire is $\angle cPx = \phi + \psi$ (same as that of the solid) :

$$\bar{u} = \overline{a\dot{\alpha}} \text{ along tangent at D to } z\text{D},$$

$$\bar{v} = \overline{b\dot{\theta}} \text{ along tangent at C to } z\text{C}.$$

So,

$$\text{T} = \tfrac{1}{2}\text{M}(a^2\dot{\alpha}^2 + b^2\dot{\theta}^2 + 2ab\dot{\theta}\dot{\alpha}) + \tfrac{1}{2}(\text{A}p^2 + \text{B}q^2 + \text{C}r^2 - 2\text{F}qr),$$

where p, q, r are the angular velocities of the suspended body about the moving axes and A, B, C are the moments of inertia given by

$$\text{A} = \Sigma m(y^2+z^2), \quad \text{B} = \Sigma m(x^2+z^2), \quad \text{and} \quad \text{C} = \Sigma m(x^2+y^2).$$

$$\text{L} = \frac{\text{K}}{2}(\phi+\psi)^2 + \text{M}g\{a(1-\cos\alpha) + b(1-\cos\theta)\}.$$

$$\therefore \quad \mathrm{T}=\tfrac{1}{2}\mathrm{M}(a^2\dot{\alpha}^2+b^2\dot{\theta}^2+2ab\dot{\theta}\dot{\alpha}) + \tfrac{1}{2}\{\mathrm{B}\dot{\theta}^2+\mathrm{C}(\dot{\phi}+\dot{\psi})^2-2\mathrm{F}\dot{\theta}(\dot{\phi}+\dot{\psi})\}.$$

So Lagrange's equations are:

$$(\mathrm{M}b^2+\mathrm{B})\ddot{\theta}+\mathrm{M}ab\ddot{\alpha}-\mathrm{F}(\ddot{\phi}+\ddot{\psi})=-\mathrm{M}gb\theta,$$
$$-\mathrm{F}\ddot{\theta}+c(\ddot{\phi}+\ddot{\psi})=-k(\phi+\psi),$$
$$\mathrm{M}ab\ddot{\theta}+\mathrm{M}a^2\ddot{\alpha}=-\mathrm{M}ga\alpha.$$

To solve the above equations we have to find the roots of the algebraic equation given by the following determinant:—

$$\begin{vmatrix} (\mathrm{M}b^2+\mathrm{B})x^2-\mathrm{M}gb & \mathrm{M}abx^2 & -\mathrm{F}x^2 \\ \mathrm{M}abx^2 & \mathrm{M}a^2x^2-\mathrm{M}ga & 0 \\ -\mathrm{F}x^2 & 0 & cx^2-k \end{vmatrix}=0.$$

This is of the form

$$\begin{vmatrix} a & h & g \\ h & b & 0 \\ g & 0 & c \end{vmatrix}=0.$$

$\therefore \quad abc-bg^2-ch^2=0$; here g and h are small.

$$a=\frac{bg^2+ch^2}{bc}, \quad b=\frac{ch^2}{ac-g^2}=\frac{h^2}{a'}, \quad c=\frac{bg^2}{ab-h^2}=\frac{g^2}{a''},$$

where a', a'' are obtained by successive approximations.

$$(\mathrm{M}b^2+\mathrm{B})x^2-\mathrm{M}gb=\frac{g^2}{c'}+\frac{h^2}{b'}$$
$$=\frac{\mathrm{F}^2\left(\dfrac{\mathrm{M}gb}{\mathrm{M}b^2+\mathrm{B}}\right)}{c\dfrac{\mathrm{M}gb}{\mathrm{M}b^2+\mathrm{B}}-k}+\frac{(\mathrm{M}ab)^2\left\{\dfrac{\mathrm{M}gb}{\mathrm{M}b^2+\mathrm{B}}\right\}^2}{\dfrac{\mathrm{M}a^2.\mathrm{M}gb}{\mathrm{M}b^2+\mathrm{B}}-\mathrm{M}ga},$$

$$\mathrm{M}a^2x^2-\mathrm{M}ga=\frac{h^2}{a'}=\frac{(\mathrm{M}gb)^2\left(\dfrac{\mathrm{M}gb}{\mathrm{M}b^2+\mathrm{B}}\right)^2}{(\mathrm{M}b^2+\mathrm{B})\dfrac{g}{a}-\mathrm{M}gb},$$

$$cx^2-k=\frac{g^2}{a''}=\frac{\mathrm{F}^2\left(\dfrac{\mathrm{M}gb}{\mathrm{M}b^2+\mathrm{B}}\right)^2}{(\mathrm{M}b^2+\mathrm{B})\dfrac{k}{c}-\mathrm{M}gb},$$

and the approximate values of the roots are

$$\frac{Mgb}{Mb^2+B}, \quad \frac{g}{a}, \quad \frac{k}{c}.$$

For sufficiently heavy solids and long wires the ratio of the torque (k) per unit twist to the moment of inertia (c) is very small and may be considered to be negligible, and the possibility of the mutual transference of torsional and pendulous oscillations therefore depends on the approximate equality of the two remaining roots, *i. e.*,

$$\frac{Mgb}{Mb^2+B} \quad \text{and} \quad \frac{g}{a}.$$

In conclusion, I wish to thank Prof. S. Purushotham, Professor of Mathematics, Maharaja's College, Vizianagaram, for his kind help in solving the problem.

Vizianagaram, South India.
April 1930.

CI. *A Note on the Fracture of Discharge-Tubes.* *By* R. H. Sloane, *M.Sc., Demonstrator in Physics, The Queen's University of Belfast* *.

[Plate XII.]

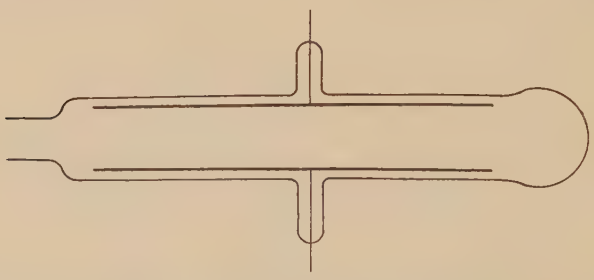
WHILST investigating the conditions of excitation near the cathode of the glow discharge in argon inconvenience was experienced from frequent spontaneous failure of the tubes. This was rather surprising, as quite gentle discharges (*e. g.* 2 milliamps. at 400 volts) were being passed. Apparently it is due partly to the use of argon, which, as is well known, gives rise to heavy cathodic sputtering, but mainly to the fact that the design of the tubes involved contact of the cathode with the walls.

The form of discharge-tube in question consisted of a length of soda-glass tubing, 27 cm. long and 3 cm. in diameter, in which were mounted two parallel sheet-nickel electrodes 22·5 × 2 cm., and 2 cm. apart, in close contact with the glass at their long edges. The design of the tube will be apparent from the accompanying figure. This tube contained pure argon at a pressure of 0·3 mm.

* Communicated by Dr. K. G. Emeléus.

Hg., and was run from the 440 volt d.c. mains with a wire resistance of 1700 ohms in series, which limited the current to about 1 ma. Conditions were varied slightly from time to time, but the current density rarely exceeded 0·1 ma. per sq. cm.

After a run of the order of twelve hours the exposed glass walls were always heavily sputtered, but usually no sign of incipient fracture was visible at this stage. More prolonged use, approximately thirty hours, however, resulted in small pieces of the sputtered film peeling away from the glass close to the cathode. The first visible sign of this was the appearance of a small spot of yellow light at a point of contact between the cathode and wall. This had a scintillating appearance. The colour was due to the sodium of the glass. The spot grew brighter and larger, and small streamers were observed to shoot out



from it along the surface of the sputtered film, leaving permanent trails from which the sputtered metal had been removed. These trails were rather long and tortuous. Once this process started it became rapidly more intense, until a fracture through the bright spot terminated the life of the tube.

An examination of the tube after fracture revealed some interesting points. Microphotographs of a piece of the glass are shown in Pl. XII. Fig. 1 (Pl. XII.) is a full-size photograph, taken by transmitted light ; the arrow points to the edge which was formed by the original fracture, the other edges being produced when the tube was opened up ; the clear triangular piece at the top was behind the cathode. Fig. 2 of the same Plate is a microphotograph ($\times$ 8·7) of part of fig. 1 ; the arrow in this case points to the edge of the cathode at which the fracture originated. Fig. 3 is an extension of fig. 2 to the

left, and fig. 4 is part of fig. 2 under higher magnification ($\times$ 21), the central part of fig. 4 being that part of fig. 3 indicated by the arrow ; the pattern towards the end of the streamers is very complicated and the curvature increases. Fig. 5 is an edge-on view ($\times$ 8·8) in the direction of the arrow in fig. 1 ; it shows how the glass was eaten away in a conical shaped hole ; presumably the crack formed when the apex of the cone had penetrated the glass. A porcelain-like material, which was apparently a nickel glass, remained in the cavity so formed, and appears white in fig. 5. Examination of this and the adjoining leaf-pattern shown in figs. 2 and 3, under high magnification, showed that it consisted of small globules of fused glass ; these do not photograph well.

It is difficult to give a satisfactory explanation of these observations. The most obvious one would seem to be that the film makes contact with the cathode, and then itself sputters, giving the pattern observed. Although perhaps explaining the trails, this fails to account for the bright spot or for the formation of the trails *subsequent* to the appearance of the bright spot. Patterns somewhat similar to these have been observed by K. G. Emeléus and F. M. Emeléus with an oxygen discharge-tube*, and were attributed at the time to oxidation of the sputtered nickel. This could hardly explain the facts in the present case, as the argon was spectroscopically free from oxygen.

Another explanation has been suggested by Dr. Emeléus as the result of some work by him and Miss J. Beck in this laboratory on the potential of the walls in the dark space†. They have found that the walls of a slightly sputtered discharge-tube are strongly positive to the discharge close to the cathode, potential differences of 200 volts being frequently found. Taking 0·01 mm. as a reasonable spacing for a poor contact, an average field of $2 \cdot 10^5$ volts per cm. would result between the cathode and wall. This might be large enough to draw an auto-electronic current from the cathode which would cause sufficient heating of the glass where it impinged on the latter to give the observed hot spot. Why this process should be aggravated by the formation of the sputtered film is not clear, except that it might increase the potential difference by increasing the conductivity of the walls

* Phil. Mag. viii. p. 383 (1929).

† To be published shortly.

between the negative glow and cathode. The conditions when the walls were heavily sputtered were not investigated by Emeléus and Beck, their tubes being never more than slightly clouded.

The streamers could be accounted for by the release of strains in the film or underlying glass, or by the existence of irregularities in the surface of the glass itself. As already mentioned, the average curvature of these streamers increases towards their ends. Fine streamers were, however, sometimes observed, extending comparatively straight along the film perpendicular to the cathode, without bright spots at their origins. The curvature may thus be influenced by the presence of the bright spot and perhaps by its effect on strains.

It is not proposed to follow up these observations systematically. Rapid failure of a tube is readily avoided, as with tubes passing heavier discharges, by suitably spacing the cathode from the wall.

CII. *Notices respecting New Books.*

The Measurement of Hydrogen Ion Concentration. By Julius Grant, Ph.D., M.Sc., A.I.C. [Pp. viii + 159 with 40 figures.] (London : Longmans, Green & Co., 1930. Price 9*s.* net.)

THE measurement of hydrogen ion concentration is of importance to many branches of industry—to brewing and other industries, which depend upon fermentation, such as bakery and sugar manufacture ; to the dyeing industry ; to the leather industry ; to the manufacture of paper ; and to agriculture. It is also of importance to the metallurgist, to the biochemist and in chemical analysis. The technique for determining the pH value has to be used by many industrial workers who do not need to have much knowledge of the theories upon which the methods are based. It is primarily for such workers that the volume under review has been written. Hitherto the industrial worker who wished to undertake the study of hydrogen ion concentration only had available for consultation books which were written for the academic student. In the present volume the theory has been treated very briefly and the controversial points have not been discussed in any detail. No previous knowledge of

electrochemistry has been assumed, so that the beginner in a strange field may safely use this volume as a guide.

The methods for the estimation of the pH valves, both the electrometric and the colorimetric methods, are explained. Full attention is given to all the practical details, and numerous pitfalls and sources of error are pointed out. Special modified methods in use for various purposes in different industries are described. A large number of selected references to the literature are given, which will be found of value by the research worker. At the end there are collected in tabular form all the data and information normally required in the estimation of pH values.

The volume undoubtedly fills a serious gap in the chemical literature, and cannot fail to prove of value to all who require to make determinations of hydrogen ion concentration.

A Treatise on Light. By R. A. Houstoun, M.A., Ph.D., D.Sc., Lecturer in Physical Optics, University of Glasgow. (Longmans, Green & Co.) Price 12*s.* 6*d.*

This book, intended for students who have been through a first-year's physics course, has now reached its sixth edition. In this edition there is some new material and a number of additional diagrams. These but enhance the value of the work which since 1915 in its various editions has held its own as one of the best text-books on Light, remarkable as much for its careful treatment of the whole range of the subject as for the systematic incorporation of the results of recent researches as they occur. We recommend the book heartily to the intelligent student.

Etoiles et Atomes. By A. S. Eddington, M.A., D.Sc., LL.D., F.R.S., Professor of Astronomy at Cambridge University. Translated by J. Rossignol, Professeur agregé de l'Université. (Price 35 francs.) (Hermann et Cie, Paris.)

It is interesting to note the appearance in French of Sir Arthur Eddington's 'Stars and Atoms.'

The translation appears to lack nothing in clearness, and will no doubt ensure that this classical work is read by as wide a public in France as it has already reached in English-speaking countries.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]

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END OF THE TENTH VOLUME.

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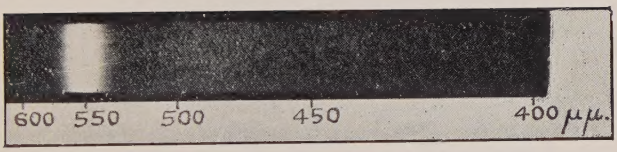
Fig. 6

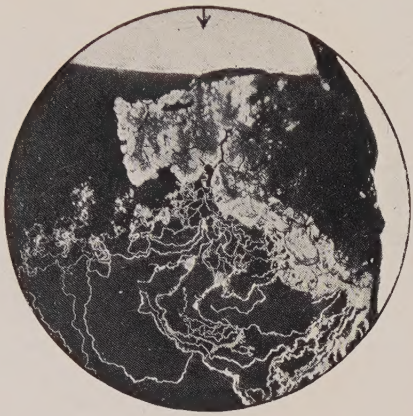


Spectrogram of glow.

Phil. Mag. Ser. 7. Vol 10, Pl. XII.

Fig. 1.

Fig. 2.



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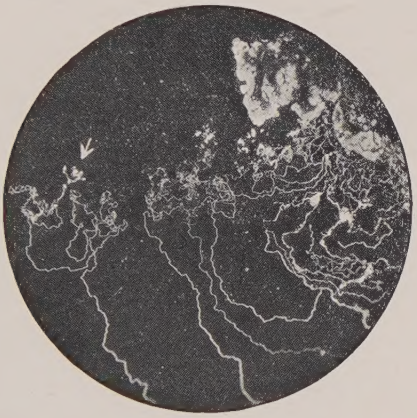

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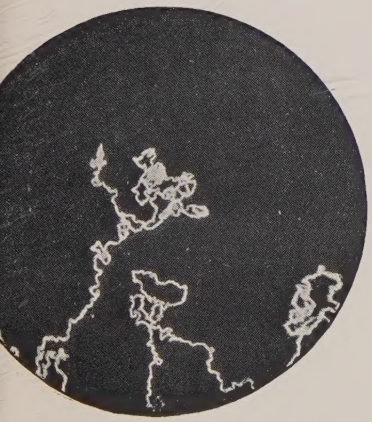

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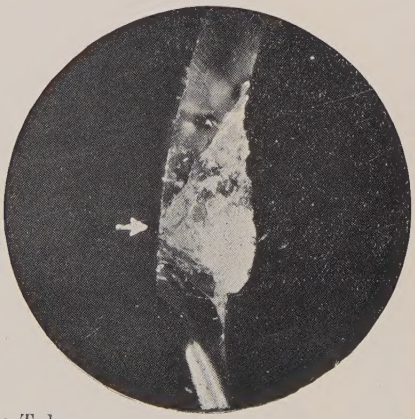

Fracture of Discharge-Tubes.